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Mathematics. — "*On* EULER's *Constant*". By Prof. J. C. KLUYVER.

(Communicated at the meeting of May 26, 1923).

In calculating the value of EULER's constant C the summation formula or any other asymptotic series is used, and one term at least in the expansion is always a transcendental quantity. It would be preferable to represent C as a convergent expression containing rational terms only, because such a representation of the number C perhaps eventually will furnish the means to establish its irrationality. As yet VACCA's series [1])

$$C = 1\left(\frac{1}{2}-\frac{1}{3}\right)+2\left(\frac{1}{4}-\frac{1}{5}+\frac{1}{6}-\frac{1}{7}\right)+$$
$$+3\left(\frac{1}{8}-\frac{1}{9}+\ldots-\frac{1}{15}\right)+4\left(\frac{1}{16}-\frac{1}{17}+\ldots-\frac{1}{31}\right)+\ldots$$

is the only result in the desired direction, and as a second I will add the proof that $C-\frac{1}{2}$ can be expanded in a convergent continued fraction

$$\frac{1}{|a_1}+\frac{1}{|a_2}+\frac{1}{|a_3}+\frac{1}{|a_4}+\ldots,$$

the quantities a_k being throughout positive and rational.

Following STIELTJES' method [2]) for converting an integral into a continued fraction, I consider the integral

$$J(z)=\int_0^\infty \frac{du}{u+z}\quad f(u)=\int_0^\infty \frac{du}{u+z}\cdot\frac{1}{e^{2\pi\sqrt{u}}-1},$$

supposing $z>0$. Expanding the integrand in powers of $\frac{1}{z}$, term-by-term integration gives the divergent series

$$\frac{c_0}{z}-\frac{c_1}{z^2}+\frac{c_2}{z^3}\ldots\ldots+(-1)^h\frac{c_h}{z^{h+1}}+\ldots\ldots,$$

the coefficients of which are determined by the equation

[1]) Q. J. Math, London, vol. XLI, p. 363.

[2]) Recherches sur les fractions continues. Oeuvres complètes, II, p. 402.

$$c_h = \int_0^\infty u^h f(u)\, du = \frac{2}{(2\pi)^{h+1}} \int_0^\infty \frac{v^{2h+1}}{e^v - 1}\, dv = \frac{B_{h+1}}{2h+2}.$$

Hence c_h, directly deduced from the Bernoullian number B_{h+1}, is a positive and rational quantity.

In order to evaluate the integral $J(z)$, we write

$$J(z) = \int_0^\infty \frac{du}{u+z} \left\{ e^{-2\pi\sqrt{u}} + e^{-4\pi\sqrt{u}} + e^{-6\pi\sqrt{u}} + \ldots + e^{-2m\pi\sqrt{u}} \right\} +$$

$$+ \int_0^\infty \frac{du}{u+z} \cdot \frac{e^{-2m\pi\sqrt{u}}}{e^{2\pi\sqrt{u}} - 1},$$

and substituting in the remainder $u = v^2$, we find

$$\int_0^\infty \frac{du}{u+z} \cdot \frac{e^{-2m\pi\sqrt{u}}}{e^{2\pi\sqrt{u}} - 1} = 2 \int_0^\infty \frac{dv}{v^2+z} \cdot \frac{v e^{-2\pi v}}{e^{2\pi v} - 1} < \frac{1}{2\pi^2 m z}.$$

Hence we have

$$J(z) = \int_0^\infty \frac{du}{u+z} \cdot \sum_{k=1}^{k=\infty} e^{-2\pi k\sqrt{u}} = \int_0^\infty du\, e^{-2\pi\sqrt{u}} \sum_{k=1}^{k=\infty} \frac{1}{u+k^2 z},$$

and, putting $u = \frac{z v^2}{4\pi^2}$, we get

$$J(z) = \int_0^\infty e^{-v\sqrt{z}}\, dv \sum_{k=1}^{k=\infty} \frac{2v}{v^2 + 4k^2\pi^2} = \int_0^\infty e^{-v\sqrt{z}}\, dv \left\{ \frac{e^v}{e^v - 1} - \frac{1}{v} - \frac{1}{2} \right\} =$$

$$= -\int_0^\infty dv \left\{ \frac{e^{-v}}{v} - \frac{e^{v(1-\sqrt{z})}}{e^v - 1} \right\} + \int_0^\infty \frac{e^{-v} - e^{-v\sqrt{z}}}{v}\, dv - \frac{1}{2\sqrt{z}} =$$

$$= -\frac{\Gamma'}{\Gamma}(\sqrt{z}) + \log(\sqrt{z}) - \frac{1}{2\sqrt{z}},$$

a result from which we deduce at once $J(1) = C - \frac{1}{2}$.

Now according to STIELTJES' theory the integral $J(z)$ can be converted formally in a continued fraction

$$\frac{1}{|a_1 z} + \frac{1}{|a_2} + \frac{1}{|a_3 z} + \frac{1}{|a_4} + \frac{1}{|a_5 z} + \ldots,$$

the quantities a_k depending on the coëfficients $c_0, c_1, c_2, \ldots$ of the

divergent series. Following the general method we consider the determinants

$$\lambda_{2n} = \begin{vmatrix} c_1 & c_2 & c_3 \dots\dots c_n \\ c_2 & c_3 & c_4 \dots\dots c_{n+1} \\ c_3 & c_4 & c_5 \dots\dots c_{n+2} \\ \dots & \dots & \dots \\ c_n & c_{n+1} & c_{n+2} \dots\dots c_{2n-1} \end{vmatrix}, \quad \lambda_{2n-1} = \begin{vmatrix} c_0 & c_1 & c_2 \dots\dots c_{n-1} \\ c_1 & c_2 & c_3 \dots\dots c_n \\ c_2 & c_3 & c_4 \dots\dots c_{n+1} \\ \dots & \dots & \dots \\ c_{n-1} & c_n & c_{n+1} \dots\dots c_{2n-2} \end{vmatrix},$$

then we shall have

$$a_1 = \frac{1}{c_0}, \quad a_2 = \frac{c_0^2}{c_1}, \dots, a_k = \frac{\lambda_{k-1}^2}{\lambda_k \lambda_{k-2}}.$$

These general formulae give no insight in the numerical values of the quantities a_k, remembering however that $c_h = \frac{B_{h+1}}{2_{h+2}}$, it is obvious that they are rational and depending on the Bernoullian numbers only. Moreover they are positive, for considering the determinant

$$D = \begin{vmatrix} c_p & c_{p+1} & c_{p+2} & \dots\dots c_{p+m} \\ c_{p+1} & c_{p+2} & c_{p+3} & \dots\dots c_{p+m+1} \\ c_{p+2} & c_{p+3} & c_{p+4} & \dots\dots c_{p+m+2} \\ \dots & \dots & \dots & \dots \\ c_{p+m} & c_{p+m+1} & c_{p+m+2} & \dots\dots c_{p+2m} \end{vmatrix},$$

with arbitrary indices p and m, we get

$$D = \frac{1}{(m+1)!} \int_0^\infty \int_0^\infty \dots \int_0^\infty f(u_1) f(u_2) \dots f(u_{m+1}) du_1 du_2 \dots du_{m+1} u_1^p u_2^p \dots u_{m+1}^p \begin{vmatrix} 1 & u_1 & u_1^2 \dots\dots u_1^m \\ 1 & u_2 & u_2^2 \dots\dots u_2^m \\ 1 & u_3 & u_3^2 \dots\dots u_3^m \\ \dots & \dots & \dots \\ 1 & u_{m+1} & u_{m+1}^2 \dots\dots u_{m+1}^m \end{vmatrix}^2$$

Hence D and in particular every determinant λ_k is positive, therefore the same conclusion holds for a_k. By direct calculation we get for the very first quantities a_k rather irregular numerical values. We shall find

$$a_1 = 12, a_2 = \frac{5}{6}, a_3 = \frac{252}{79}, a_4 = \frac{79^2}{60 \cdot 241}, a_5 = \frac{241^2 \cdot 11 \cdot 12}{79 \cdot 52489},$$

but these results give no indication about the possible convergence of

the continued fraction. In order to prove this convergence for $z > 0$, we change $f(u)$ into

$$g(u) = \frac{1}{e^{2\pi\sqrt{u}} - e^{-2\pi\sqrt{u}}}$$

and applying STIELTJES' method to the new integral

$$J_1(z) = \int_0^\infty \frac{du}{u+z}\, g(u) = -\frac{\Gamma'}{\Gamma}(\sqrt{z}) + \frac{\Gamma'}{\Gamma}(2\sqrt{z}) - \frac{1}{4\sqrt{z}} - \log 2,$$

we obtain the continued fraction

$$\frac{1}{|a'_1 z} + \frac{1}{|a'_2} + \frac{1}{|a'_3 z} + \frac{1}{|a'_4} + \frac{1}{|a'_5 z} + \ldots.$$

with $a'_{2n} = \frac{1}{2n}$ and $a'_{2n+1} = \frac{16}{2n+1}$. Now both the series $\sum_1^\infty a'_{2k}$ and $\sum_0^\infty a'_{2k+1}$ evidently, diverge, hence we infer that for $z > 0$ the new continued fraction necessarily converges, and by the way we may note for $z = \frac{1}{16}$ the rather remarkable result

$$\frac{\pi}{2} - 1 = \frac{1}{|\frac{1}{1}} + \frac{1}{|\frac{1}{2}} + \frac{1}{|\frac{1}{3}} + \frac{1}{|\frac{1}{4}} + \ldots.$$

Comparing the functions $f(u)$ and $g(u)$ we have

$$\frac{f(u)}{g(u)} = 1 + e^{-2\pi\sqrt{u}}$$

and accordingly everywhere in the range of integration

$$1 \leqq \frac{f(u)}{g(u)} \leqq 2,$$

therefore, again using STIELTJES' argument, we conclude to the inequalities

$$\tfrac{1}{2}(a'_1 + a'_3 + a'_5 + \ldots + a'_{2n+1}) < (a_1 + a_3 + a_5 + \ldots + a_{2n+1}) < \\ < (a'_1 + a'_3 + a'_5 + \ldots + a'_{2n+1}),$$

otherwise written

$$8\left(\frac{1}{1} + \frac{1}{3} + \frac{1}{5} + \ldots + \frac{1}{2n+1}\right) < (a_1 + a_3 + a_5 + \ldots + a_{2n+1}) < \\ < 16\left(\frac{1}{1} + \frac{1}{3} + \frac{1}{5} + \ldots + \frac{1}{2n+1}\right).$$

Consequently the lower limit of a_{2k+1} must be zero, and that agrees with the fact that $\frac{c_{n+1}}{c_n}$ tends to infinity, for STIELTJES shewed that in that case no upper limit can be assigned to $\frac{1}{a_n a_{n+1}}$.

The principal conclusion, however, is that the series $\sum_0^\infty a_{2k+1}$ diverges, that therefore the continued fraction

$$\frac{1}{|a_1 z} + \frac{1}{|a_2} + \frac{1}{|a_3 z} + \frac{1}{|a_4} + \frac{1}{|a_5 z} + \cdots$$

converges except when z is real and negative, and that it is equal to the integral $J(z)$. Thus then, putting $z = 1$, we have proved that $C - \frac{1}{2}$ can be expanded in the continued fraction

$$\frac{1}{|a_1} + \frac{1}{|a_2} + \frac{1}{|a_3} + \frac{1}{|a_4} + \frac{1}{|a_5} + \cdots,$$

the quantities a_k being rational and positive, whilst those of odd index have the lower limit zero. More or less we are inclined to believe that a fraction satisfying these conditions cannot represent a rational number, and so the expansion of $C - \frac{1}{2}$ again suggests the conjecture that C must be irrational.

The result obtained is of no practical value; that after some reductions we have

$$C - \tfrac{1}{2} = \frac{1}{|12} + \frac{6}{|5} + \frac{79}{|42} + \frac{2410}{|79} + \frac{262445}{|2651} + \cdots,$$

is of small service in the evaluation of the constant, and though numerator and denominator of any convergent can be expressed in the Bernoullian numbers, in approximating the constant C other methods are to be preferred.

Chemistry. — "*Researches on the Addition of Water to Ethylene and Propylene*". (Preliminary Communication). By Dr. J. P. WIBAUT and J. J. DIEKMANN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of March 24, 1923).

About two years ago experiments were carried out by one of us purposing to study the possibility of a direct addition of water to ethylene and propylene. The continuation of this investigation has been rendered possible by a liberal support granted me from the HOOGEWERFF-fund. I gladly avail myself of this opportunity to express my great indebtedness to the Board of Management of the HOOGEWERFF-fund for this help.

Though these investigations have not yet been completed, it seems desirable to me in connection with a short notice in the „Chemiker Zeitung" of Jan. 2nd 1923 (N°. 47, p. 7), in which H. W. KLEVER describes similar researches, to publish a preliminary communication on the results obtained by us.

J. P. WIBAUT.

§ 1. *The Action of Water-vapour on Ethylene and Propylene in the Presence of Catalysts.*

Since the investigations by IPATIEW, SENDERENS and SABATIER it has been known that at high temperature and in the gaseous condition ethyl-alcohol and some of its homologues can be decomposed in two ways:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I).$$

$$C_2H_5OH \rightarrow CH_3\overset{H}{C}{=}O + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II).$$

Both reactions are typical catalytic reactions, which only proceed readily in the presence of certain contact-substances. Anhydrous aluminiumsulphate and aluminiumoxide are typical catalysts that split off water (reaction I). Metals like copper and iron, especially in finely divided condition, are typical catalysts for the splitting off of hydrogen (reaction II).

The range of temperature, in which particularly the first reaction

takes place, lies between 300—400°, dependent on the nature of the catalysing substance; when the temperature is raised to about 400° and higher, the formation of aldehyde becomes prominent even in the presence of substances like aluminium oxide and other catalysts that split off water.

It is well known that reaction (II) is reversible — aldehydes can be smoothly reduced with molecular hydrogen over nickel — but nothing is known about the reversibility of reaction (I).

In the extensive literature on the splitting up of alcohols into olefine and water, the question whether direct addition of water to the double bond in ethylene and propylene is actually possible, has never been examined. We have carried out a number of experiments to answer this question. A mixture of ethylene and water-vapour was led over different contact-substances at a temperature between 300° and 400° C. On use of aluminiumhydroxyde or of aluminium sulphate as catalysts, the reaction product contained acetaldehyde. We have proved the presence of acetaldehyde by the usual reactions (reduction of an ammoniacal solution of silver hydroxide); SCHIFF's reaction; reaction with nitro-prussidsodium and piperidine according to LEWIN) and also isolated as p-nitrophenylhydrazone. The quantities of acetaldehyde are very small; by far the greater part of the ethylene remains unchanged during the experiment. The quantity of acetaldehyde amounted to from 0,2 to 0,4 % at 350°—360°, calculated to the quantity of ethylene.

The presence of alcohol could not be verified [1]).

In our opinion the formation of acetaldehyde must be explained in this way that primarily ethylalcohol is formed through addition of water to ethylene, and then acetaldehyde through splitting up of hydrogen. If this second reaction proceeds much more rapidly than the addition of water to the double bond, no alcohol will be found in the reaction product. As at 350°—360° ethyl-alcohol is almost quantitatively decomposed into ethylene and water (at this temperature, however, a little hydrogen is also formed) it is clear that only at a lower temperature the inverse reaction can take place in a considerable degree. We have, however, not succeeded in finding a catalyst that causes the addition of water to ethylene below 300°.

We have proved by means of a separate experiment that no acetaldehyde is formed from mixtures of dry ethylene with about 10% of air at 360° over aluminiumoxide. It, therefore, appears from

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[1]) The analytical particulars will be given later, as also the full description of the arrangement of the experiments.

this that the formation of acetaldehyde is not the consequence of an oxidation of ethylene, e. g. according to the scheme

$$C_2H_4 + O \rightarrow \underset{\diagdown O \diagup}{CH_2—CH_2} \rightarrow CH_3\overset{H}{C}=O$$

Hence the formation of acetaldehyde cannot have been caused by the possible presence of small quantities of air in the ethylene used.

We are, therefore, of opinion that we are justified in concluding that a primary addition of water to the double bond has taken place, and that the reaction:

$$C_2H_5OH \rightleftarrows C_2H_4 + H_2O$$

may accordingly be considered as a reversible reaction.

We have obtained perfectly analogous results with mixtures of propylene and water-vapour. At 350° and in the presence of aluminiumhydroxide *acetone* was then formed in a quantity of from 0,2 to 0,3 % of the propylene. In our opinion the primary formation of isopropylalcohol by addition of water to propylene, must be assumed in this case. Afterwards the isopropylalcohol is transformed to acetone through the splitting off of hydrogen. Hence the direct addition of water proceeds analogously to the addition of hydriodic acid, in which likewise the isopropyl compound appears. Accordingly the rule of MARKONIKOW remains valid also in this case.

On the ground of these results it is probable that the addition of water to propylene and ethylene can take place under high pressure at temperatures far below 300°. We have, however, made no experiments in this direction.

§ 2. *The Hydration of Ethylene and Propylene by Means of Acids.*

The syntheses of ethyl- and isopropylalcohol from ethylene and propylene by the formation of alkyl-sulphuric acid, and subsequent hydrolysis, by M. BERTHELOT [1]) are among the classic syntheses of organic chemistry. BERTHELOT investigated the absorption of these olefines by pure sulphuric acid of 98—99 % H_2SO_4 at ordinary temperature. Afterwards the absorption of ethylene by sulphuric acid has been repeatedly studied. Particularly in the last few years several technical chemists have made experiments to absorb the ethylene from

[1]) BERTHELOT: Chimie organique fondée sur la synthèse, p. 115. c. f. Ann. de Chimie et de Physique. (7), 4, 101 (1895). Bull. Soc. Chim. XI, 13. (1869).

coal-distillation gases by means of hot strong sulphuric acid (of 96 %), and to obtain ethylalcohol after dilution and distillation of the sulphuric acid [1]).

With regard to the action of sulphuric acid on propylene, a process of CARLETON-ELLIS [2]) has become known. In this process the waste gases formed in the preparation of light hydrocarbons from heavy petroleum-distillates (cracking-process of BURTON) are passed through sulphuric acid of 87 %; the propylene present in these is said to be transformed into isopropylsulphuric acid. After dilution and distillation of the sulphuric acid isopropylalcohol is obtained.

Systematic researches on the behaviour of ethylene and propylene towards acids of different concentrations have not been published.

On the other hand there are many instances known, in which the addition of water to a double bond takes place under the influence of diluted acids. Geraniol absorbs two molecules of water when treated with 5 % sulphuric acid. BUTLEROW [3]) found that isobutylene and heptylene were very slowly hydrated to the corresponding alcohols by means of diluted sulphuric acid and nitric acid at the ordinary temperature.

It seemed interesting to us to examine how ethylene and propylene would behave towards acids of different concentrations. If ethylsulphuric acid can be obtained through the action of ethylene on diluted sulphuric acid at high temperature, there would be a possibility that afterwards the ethylsulphuric acid should be hydrolized:

(1) $$C_2H_4 + H_2SO_4 \rightarrow C_2H_5HSO_4$$

(2) $$C_2H_5HSO_4 + H_2O \rightarrow C_2H_5OH + H_2O$$

If the two reactions proceeded rapidly enough, the experiment might be arranged so that the alcohol formed is immediately distilled off from the reaction liquid.

Such a course of the reaction would then be practically an addition of water to ethylene, in which the question whether we have to do here with a direct addition or which an intermediary

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[1]) FRITZSCHE. Chemische Industrie **20**, 266 (1897) and **21**, 27 (1898); TAU and BERTELSMANN, Glück Auf **57**, 189 (1921); BURY en OLLANDER: „Byproduct development in the Iron and Steel Industry"; Paper read before the Cleveland Institution of Engineers, 15 December 1919; cf. TIDMAN, Journ. Soc. Chem Ind. **40**, 86 T (1921); DE LOISY. Compt. Rend. Ac. d. Sc. Paris **170**, 50 (1920); DAMIENS, DE LOISY en PIETTE, Eng. Pat. 180988 (1922).

[2]) Cf. Chemical and Metallurgical Engineering. Vol. **23**, 1230 (1920).

[3]) Lieb. Ann. **180**, 245 (1876).

formation of ethylsulphuric acid, can be left undecided for the present.

We have devised an apparatus, in which an ascending stream of gas came into intimate contact with the descending acid. This washing apparatus, which is placed vertically was electrically heated by means of a coil of nichrome-wire so as to make it possible to keep the reaction temperature constant within narrow limits. The ethylene, which is led through the heated, diluted sulphuric acid will withdraw water-vapour from the liquid, for so far as it is not absorbed, which would cause the acid to become more concentrated in the course of the experiment. To prevent this we have added water-vapour to it at the same time with the ethylene; the partial tension of the water-vapour in the introduced gas-mixture was about the same as the water-vapour tension of the used sulphuric acid at the temperature of the experiment. In this way the concentration of the sulphuric acid was kept about constant during the experiment.

At the top of the apparatus there escaped, therefore, water-vapour, not absorbed ethylene, and alcohol vapour, if any was formed.

It actually appeared possible to obtain alcohol from ethylene in this way. A mixture of ethylene and steam was washed with sulphuric acid of 65 % H_2SO_4 at a temperature of 150°—160°. After 5 litres of ethylene had been passed through in 5 hours' time, the distillate contained 0,21 gr. of alcohol [1]), i. e. a conversion of about 2 %.

Then the sulphuric acid used was strongly diluted and distilled out, and in this way 0,08 gr. of alcohol more was obtained. Hence a little ethylsulphuric acid was still present in the sulphuric acid after the experiment. This renders it probable that the ethylsulphuric acid is formed as an intermediate product, and that accordingly the formation of alcohol is the result of two successive reactions, as given above.

In a second similar experiment 4 % of the ethylene that was passed through, was converted into ethylalcohol.

With a mixture of sulphuric acid and water containing 55 % H_2SO_4 only 0.01 gramme of ethylalcohol was found in the distillate, when 5 litres of ethylene mixed with steam had been passed through at 140°.

With sulphuric acid of 70 % no alcohol was found in the distillate, when three litres of ethylene had been passed through. After

[1]) The analysis took place by oxidizing the reaction liquid with chromic acid, in consequence of which the alcohol present was oxidized to acetaldehyde. This latter was determined colorimetrically.

dilution and distillation the sulphuric acid yielded, however, 0.32 gr. of alcohol, which was, therefore, present as ethylsulphuric acid. This corresponds with a conversion of 5 %.

In these experiments most of the ethylene passed unchanged through the sulphuric acid; only a slight carbonisation took place. Though in principle it, therefore, appears possible to convert ethylene in this way into ethylalcohol, the yield was so small that no practical significance can be assigned to these experiments.

These researches are being continued with other acids and with salts, as aluminiumsulphate and others.

§ 3. *Propylene and Sulphuric Acid.*

It is well known from BERTHELOT's investigations that propylene is very rapidly absorbed at the ordinary temperature by sulphuric acid of 98—99 %. We have first of all made some preliminary experiments on the action of sulphuric acid of different concentrations on propylene.

In a HEMPEL's gas-pipette 100 cc propylene was placed together with the sulphuric acid to be examined.

Sulphuric acid of 96 % at once absorbs the propylene, also sulphuric acid of 90 % acts very rapidly on it; with acid of 85 % the propylene is absorbed after 20 minutes' shaking, about an hour being required for this with acid of 80 %. Also sulphuric acid of 75 % still absorbs propylene, but very slowly.

We have further investigated the action of propylene on sulphuric acid of 96 % at 0°, in which we carefully guarded against rise of temperature both during the absorption of the gas, and during the pouring out of the reaction product on ice. We have only succeeded in obtaining a small quantity of isopropylalcohol from the reaction product.

Through the action of the sulphuric acid the bulk of the propylene was changed into an oily liquid, which was unsaturated, and boiled within wide limits. It is, therefore, probable that higher unsaturated hydro-carbons are formed by the condensing action of the sulphuric acid. BERTHELOT too states that such condensation products are formed, when rise of temperature takes place during the experiment. In our experiments with sulphuric acid of 96 % at 0° the bulk of the propylene was always transformed into condensed and resinous products in spite of all our precautions. With sulphuric acid of 85 % the absorption of propylene takes place very slowly at 10°. On further treatment

of the reaction product, chiefly condensation products were again obtained.

We then examined the absorption of propylene by more diluted sulphuric acid at higher temperature. The experiments were arranged in the same way as was already described for ethylene. The mixture of propylene and steam was brought in contact in counter-current with sulphuric acid of definite concentration and definite temperature in the vertical washing-apparatus; 7.5 litres of propylene mixed with steam were passed in 4 hours through sulphuric acid of 55 % H_2SO_4 at 140°. The distillate contained 0.25 gr. isopropyl alcohol. After dilution with water a distillate was obtained from the acid in which 0.27 gr. of isopropylalcohol [1]) was present. There was, therefore, evidently still isopropylsulphuric acid present in the acid. In all 2.6 % of the total quantity of propylene was, accordingly, obtained as isopropyl alcohol.

A much greater part of the propylene was, however, decomposed. Separation of carbon took place and formation of sulphur-dioxide. After the experiment 5,3 litres of the 7,5 litres of propylene was found back. Hence 9 % of the consumed quantity of propylene was changed into isopropyl alcohol.

An experiment with sulphuric acid of 45 % H_2SO_4 and at 125—130° proceeded in the same way; 6 litres of propylene were passed through, 5 litres of them were obtained after the experiment. The yield of isopropyl alcohol amounted to 0,2 gramme in the distillate and 0.1 gramme in the acid liquid, together 0,30. gr. i.e. 10 % of the consumed propylene. Here too a large part of the consumed propylene was carbonised.

It therefore, appears from these experiments that the hydration of propylene by hot diluted sulphuric acid is possible. The reaction velocity, however, is small, which renders the yield small. Besides the sulphuric acid has a decomposing action on the propylene. If on the other hand the experiment is made with concentrated sulphuric acid at low temperature, the propylene is quickly attacked, but chiefly transformed into condensation products.

We have tried therefore the action of other acids. We first investigated the action of benzene sulphonic acid. 6 litres of propylene with steam were passed through a concentrated solution of benzene sulphonic acid; in the aqueous distillate of this experiment we found 0,25 gr. isopropyl alcohol or about 1½ % of the propylene. Hence in this case too the reaction proceeds slowly.

[1]) The analysis took place by oxidation to acetone, and colorimetric determination of this substance.

The result of the experiments on the action of acids on ethylene and propylene can, therefore, be summarized as follows: It is possible to obtain ethyl alcohol, resp. isopropyl alcohol by one operation from ethylene and propylene by means of mixtures of sulphuric acid and water at 130—150°. In this reactions the alkylsulphuric acids are probably formed as intermediate products.

The yield of alcohols is, however, very small, and particularly with propylene, the hydro-carbon is decomposed in another way during the experiment. These investigations are being continued.

Physics. — *"The relation between the widening and the mutual influence of dispersion lines in the spectrum of the sun's limb."* By Prof. W. H. JULIUS and Dr. M. MINNAERT.

(Communicated at the meeting of April 28, 1923).

Introduction.

The hypothesis that the darkness of Fraunhofer lines is mainly an effect of anomalous dispersion enables one to explain, at any rate qualitatively, a great many characteristics of the solar spectrum. It thus appears possible to formulate a theoretical connection — which has then of course to be verified quantitatively — between numerous phenomena that are less easily seen as inter-dependent if we consider them from the point of view of the unmodified classical absorption theory introduced by KIRCHHOFF. Such phenomena are e.g.: the general displacement of the solar lines towards the red, differing greatly in amount from line to line; the limb-centre displacements and their dependence on intensity and wave-lenght; the widening and the change of intensity of the lines as the limb is approached; the apparent mutual repulsion of neighbouring Fraunhofer lines, generally greater at the limb than in the centre of the disk; the systematically curved shape of the lines of the spot-spectrum if the slit cuts the spot in a direction passing through the centre of the disk; the gradual increase of the distance between the components of the bright calcium lines H_2 and K_2 as the limb is approached; and various particulars of a more local character.

We shall endeavour to express mathematically the connection which, according to the dispersion theory, should exist between a few of the above-mentioned phenomena, and then to investigate how far these quantitative relations agree with the results of measurements made on solar lines.

It is evident that the *absolute magnitude* of the influence exercised by anomalous dispersion in the solar gases on the aspect of Fraunhofer lines cannot be calculated *directly* so long as the refracting and scattering power of the sun is not otherwise known. Neither can this power be safely computed starting from line displacements only. It must be remembered, however, that a similar uncertainty prevails regarding the values given for temperatures, pressures, radial velocities, intensities of magnetic or electric fields, or grades of dissociation in the sun in so far as such values are derived from

spectral phenomena; in fact, such statements are always based on the doubtful assumption that the observed spectral phenomena are entirely due to the causes mentioned. There is, of course, no objection to introducing this assumption, — provided its hypothetical character be always kept in mind.

With equal justification we may assume that Fraunhofer lines are mainly "dispersion lines"; the essential point will then be to examine whether the deductions from this hypothesis result in an adequate theory, covering a substantial proportion of observational data. In this paper we confine ourselves to showing that the dispersion theory of the solar spectrum connects quantitatively two at first sight independent groups of observed phenomena, namely the well-established general *widening* of the Fraunhofer lines at the limb, and the increase, also at the limb, of the *mutual influence* of neighbouring lines. This relation proves to be independent of the unknown laws that govern the weakening of any given kind of light on its way through the solar gases; it enables us to indicate an *upper limit* of the mutual influence that may be expected, thus lending fresh support to our fundamental hypothesis. It will be shown, indeed, that the average value of the mutual influence as deduced from the dispersion theory is perfectly consistent with the actual observations.

The dispersion lines which, according to our hypothesis, envelop the exceedingly narrow [1]) true absorption lines of the solar spectrum arise from two dimming processes, viz.: irregular refraction and molecular scattering. For although light of *any* wave-length is subject to refraction and scattering on its long way through selectively absorbing gases, it is well known that these causes of darkening specially affect waves in the immediate vicinity of absorption lines. As the two processes weaken the transmitted light according to different laws, we shall treat them separately.

I. On the weakening of light in passing through extensive masses of gas.

§ 1. *Spreading of light by irregular ray-curving in a mixture of gases.*

Suppose we have in a given space a mixture of gases which, if they were each of them alone to fill the space, would show the absolute refractive indices n_1, n_2 .... n_i ....; then, according to ex-

[1]) Our assumption that real absorption is restricted to *very* small ranges of wave-lengths is in harmony with views recently derived from the quantum theory by N. Bohr (Zeitschr. f. Physik **13**, 162, 1923).

periments of BIOT and ARAGO (confirmed by modern observations), the refracting power of the mixture equals the sum of the refracting powers of the constituents:

$$n - 1 = \Sigma (n_i - 1).$$

The condition is implied that the gases do not act on each other. We shall assume this law to be valid also in those spectral regions where one of the constituents causes anomalous dispersion, although no very accurate direct measurements concerning such cases are as yet available. (The exceedingly narrow regions of true absorption are not considered here).

If the gaseous mass is very extensive and of unequal optical density, with irregular gradients in all directions, it will make every beam of light spread out like a bunch of feathers. According to ORNSTEIN and ZERNICKE [1]) the rate of this kind of scattering is determined by "the average square of the spreading per unit of length" $\frac{\alpha^2}{l}$; to any short path l corresponds an angle α depending on the average value of the irregular density gradients, and proportional to $n-1$ of the mixture. The weakening of the transmitted light will therefore be a function of

$$(n-1)^2 = [\Sigma (n_i - 1)]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

that has the property of increasing and decreasing with this quantity. A characteristic difference between scattering by irregular refraction, and molecular scattering, is, that in the latter process a considerable part of each beam passes straight, and a small part of it disperses in all directions, whereas in refractional scattering every beam itself widens like a plume.

§ 2. *Scattering of light by the molecules of a gaseous mixture.*

If a beam of light of intensity I_0 has travelled a distance z through a medium containing N scattering particles per cube cm., its intensity has diminished to $I = I_0 e^{-hz}$, where, according to RAYLEIGH, h has the value

$$h = \frac{32 \pi^3 (\nu - 1)^2}{3 N \lambda^4}.$$

In this expression ν is explicitly stated to represent the refractive index of the medium as modified by the scattering particles against the unmodified medium [2]). Denoting the absolute index of the latter

[1]) ORNSTEIN and ZERNICKE, These Proceedings, Vol. 21, p. 115 (1917).

[2]) RAYLEIGH, Phil. Mag. **47**, 375, 1899. — Scientific Papers IV, 400.

by n, the absolute index of the modified medium by n', we have

$$h = \frac{32\,\pi^3\left(\frac{n'}{n}-1\right)^3}{3\,N\,\lambda^4} = \frac{32\,\pi^3\,(n'-n)^3}{3N\,\lambda^4\,n^3} = \frac{32\,\pi^3\,(n'-n)^3}{3N\,\lambda^4}$$

because for thin gases we may put $n^3 = 1$.

We shall take for granted that this expression for h remains valid in those regions of the spectrum where the scattering particles produce anomalous dispersion. It is precisely in those regions that h will assume considerable values.

Now suppose there be a mixture consisting of $N_1, N_2, \ldots N_i, \ldots$ scattering particles of the kinds $1, 2, \ldots i, \ldots$ For each kind the mixture of the *remaining* kinds forms the "unmodified medium", whilst the "modified medium" is the same in all cases, viz. the complete mixture. We are concerned, therefore, with a single quantity n' and several values $n_{(1)}, n_{(2)}, \ldots n_{(i)}, \ldots$ of n, if $n_{(i)}$ denotes the absolute refractive index of the mixture without the constituent i.

The scattering-coefficient h of the complete mixture will be the sum of the scattering-coefficients peculiar to the separate constituents, each in its proper medium:

$$h = h_1 + h_2 + \ldots h_i + \ldots = \frac{32\,\pi^3}{3\,\lambda^4}\,\Sigma\,\frac{(n'-n_{(i)})^2}{N_i}$$

This expression may be simplified because the above-mentioned law of Biot and Arago requires, that

$$n'-1 = (n_{(i)}-1) + (n_i-1)$$

n_i representing the absolute refractive index which the gas i would show if it were alone in the given space. We, therefore, have $n'-n_{(i)} = n_i-1$, and may write:

$$h = \Sigma\,h_i = \frac{32\,\pi^3}{3\,\lambda^4}\,\Sigma\,\frac{(n_i-1)^2}{N_i}.$$

A beam of light, having travelled a long way through such a mixture of gases, will emerge with a loss of intensity expressible as a certain function of h which has the property of increasing and decreasing with h. In regions of the spectrum sufficiently small to permit of neglecting the change of λ^4 in them, we see that now

$$\Sigma\,\frac{(n_i-1)^2}{N_i} \quad \ldots\ldots\ldots \quad (2)$$

is the variable quantity determining the loss of light. (Compare this expression (2) with the corresponding one (1) which applies to refractional scattering).

§ 3. *How anomalous refraction and anomalous scattering act in producing dispersion lines.*

It appears from the above remarks that the distribution of the intensity in a dispersion line is determined by two darkening laws which, it is true, depend on local circumstances (dimensions and shape of the source of light, condition of the medium, etc.), and to that extent are unknown, but which we do know will change with *wave-length* in accordance with the functions (1) and (2). We shall first deal with the share which irregular refraction, and thereafter with the share which molecular scattering has in the formation of dispersion lines.

A. Imaginary pure refraction lines.

Imagine a selectively absorbing gaseous mixture, lacking the faculty of molecular scattering, but with many irregular gradients of density; let a beam of white light travel through that medium, and attention be confined to a small part of the spectrum where only one characteristic frequency, i.e. one ideally sharp absorption line, is in evidence.

If the said line were absent, the mixture would, in this narrow range of wave-lenghts, show a refracting power n_0—1 varying only very slowly with λ, but to this will now be added the anomalous refracting power n_1—1 of the constituent producing the absorption line, thus determining the resultant refracting power:

$$n - 1 = (n_0 - 1) + (n_1 - 1).$$

The term (n_0—1) will, as a rule, preserve the same (generally positive) sign throughout the region considered, whereas (n_1—1) is negative on the violet side of the line, positive on the red side. Light on the violet side of a line will be called V-light, on the red side R-light. All effects of refraction in a gaseous mixture are, therefore, on an average greater for R-light than for V-light, because they depend on $(n-1)^2$ or on the *absolute* value of n—1, i.e. on $|(n_0-1)+(n_1-1)|$.

Fig. 1*a* shows the course of n_0—1 and n_1—1 each separately; Fig. 2*a* gives $n-1=(n_0-1)+(n_1-1)$; in Fig. 3*a* is represented the course of $|n-1|=|(n_0-1)+(n_1-1)|$ which determines the distribution of the light in our "refraction line".

The sharp absorption line will thus be enveloped in an *asymmetric* refraction line, whose "centre of gravity" is displaced towards the red if n_0—1 has the positive sign.

(The general displacement of the Fraunhofer lines towards the

red, which increases on approaching the sun's limb, may be considered in connection with these inferences).

Let us now imagine our small spectral region to contain *two* neighbouring sharp absorption lines, then we have:

$$n-1 = (n_0-1) + (n_1-1) + (n_2-1),$$

where n_0-1 is again assumed to be nearly constant, and the other two terms are strongly variable with λ. In the region between the lines, (n_1-1) and (n_2-1) have opposite signs (cf. Fig. 1,*b*, where the three terms are represented separately). The resultant $n-1 = f(\lambda)$

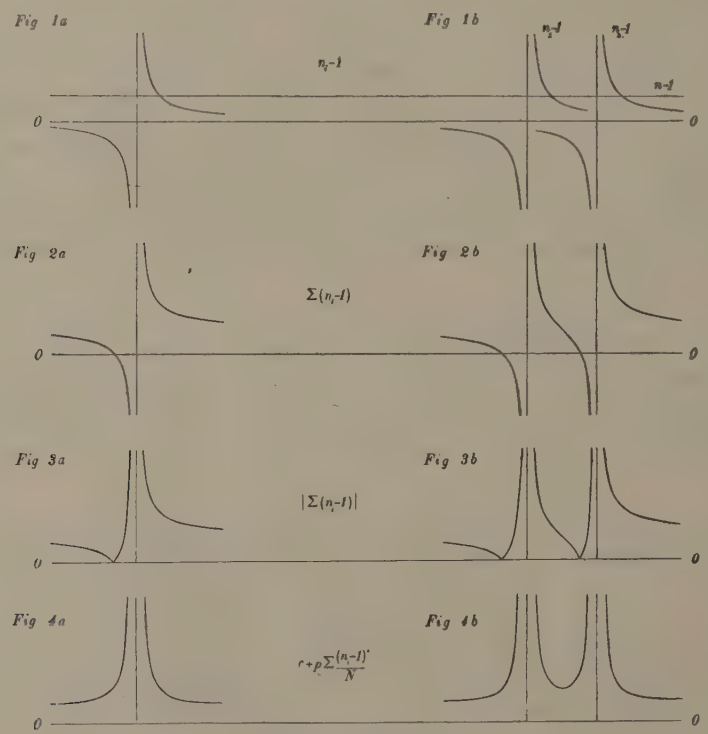

Fig. 1*a*—4*b*.

shows a point of inflexion there (Fig. 2,*b*); and, owing to the opposite signs of (n_1-1) and (n_2-1), the modulus $|(n_0-1)+(n_1-1)+(n_2-1)|$ is smaller than $|(n_0-1)+(n_1-1)|$ in the left section, and smaller than $(n_0-1)+(n_2-1)|$ in the right section of the interval (cf. Fig. 3,*b*), so that on the two sides of the refraction lines that face each other the weakening of the light is less than it would be if the lines stood wide apart. The "centres of gravity" of two neighbouring refraction lines are, therefore, a little more

distant from each other than their cores, i.e. the true absorption lines: we observe an apparent repulsion.

In Fig. 3 we see, moreover, that on the violet side of each line there appears a point where $n-1=0$. (If n_0-1 were negative, such a point would be found on the red side of the line). Light of the corresponding wave-length would not be weakened by irregular refraction and should, therefore, show an intensity in the spectrum, surpassing the average intensity of regions clear from lines. JEWELL[1]) seems indeed to have observed casually such phenomena in the solar spectrum. It is not surprising, however, that similar places of greater brillancy are not very conspicuous there; for we can scarcely doubt that in the sun the proportion of the components of the mixture varies with depth, so that the values of λ for which $n-1=0$ will not be the same on the entire paths of the beams. Moreover, the Fraunhofer lines are partly due to molecular scattering, and it will presently be shown that this process does not involve the appearance of such narrow regions of greater brillancy in the spectrum (at least not in the central parts of the solar disk). Both circumstances tend to obliterate the brighter places near refraction lines.

B. Imaginary pure scattering-lines.

Now suppose the density of a gaseous mixture to be so uniform, that rays of light pass through it in straight lines, then the true absorption lines will *yet* be enveloped into dispersion lines, because for kinds of light belonging to the nearest environment of the distinctive frequenties the coefficient of molecular scattering has greater values. Let us analyse, indeed, how

$$h=\Sigma h_i=\frac{32\pi^3}{3\lambda^4}\Sigma\frac{(n_i-1)^2}{N_i}$$

varies with λ in a narrow spectral region containing a single absorption line of the constituent j. All terms of the sum but one may there be treated as constants, so that

$$h=C+\frac{32\pi^3}{3\lambda^4}\cdot\frac{(n_j-1)^2}{N_j}.$$

This quantity varies with λ in the manner represented in Fig. 4,*a*; the curve is symmetrical with respect to the absorption line, provided that the dispersion curve associated with the line has the regular

[1]) JEWELL, Astroph. Journ. III, 99, 1896. Cf. also: ABBOT, The Sun, p. 115, where analogous observations of EVERSHED are mentioned in addition.

shape, and that the change of λ^4 in the small region may be neglected. The distribution of the light in the scattering line will then also be symmetrical; this we may infer without knowing the exact form of the law of darkening [1]).

In contrast to what characterizes pure refraction lines, the symmetry of pure scattering lines is *not* disturbed by the addition of a similar cause of weakening that is constant in the region considered. (The above expressions (1) and (2) explain this difference).

Anomalous molecular scattering, or diffusion of light, cannot therefore have any share in the production of the general displacements of the solar lines towards the red [2]).

Let us now consider the case that our small spectral region contains *two* absorption lines. The scattering coefficient will then take the form

$$h = C + p\left[\frac{(n_j-1)^2}{N_j} + \frac{(n_k-1)^2}{N_k}\right],$$

for we may replace the factor $\frac{32\pi^3}{3\lambda^4}$ by the constant quantity p. Fig. 4*b* represents h as a function of λ. To this will correspond a darkening curve whose ordinates grow and decline with h. We see that in the interval between the absorption lines the superposition of their individual scattering effects must produce a greater increase of the darkening than outside the pair; so the centres of gravity of the two diffusion-lines will be a little less distant from each other than the absorption lines proper (apparent attraction).

Summarizing the above qualitative results with a view to their application in the spectroscopy of celestial bodies, we may state:

1. The general but very unequal displacements of the Fraunhofer-lines towards the red can be explained by the properties of refraction lines, but not by those of diffusion lines. This also applies to the limb-centre displacements.

2. The mutual influence of neighbouring Fraunhofer lines, which increases, as a rule, from the centre towards the limb of the solar disk, may be the result of either scattering process; but irregular refraction causes apparent repulsion, molecular diffusion of light gives apparent attraction.

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[1]) The law of darkening through molecular scattering in the sun has been amply studied by J. SPIJKERBOER in a dissertation, published in Utrecht, 1917; cf also Arch. néerl. IIIA, 5, p. 1—115, 1918.

[2]) To this point our attention has first been drawn in a conversation with EINSTEIN.

II. The relation between width and mutual influence in dispersion lines and in Fraunhofer lines.

In this chapter formulae will be deduced expressing the connection between mutual influence and width of dispersion lines. If Fraunhofer lines are in the main dispersion lines, it will thus be possible, starting from data concerning the widening of the lines in the spectrum of the sun's limb, to derive values for the probable increase of the mutual influence in passing from the centre to the limb. We may then compare these theoretical results with the data obtained from observations regarding limb-centre displacements of Fraunhofer lines.

The respective shares which irregular refraction and molecular scattering may have in the production of the lines will again be treated separately.

§ 1. *Refraction lines in the spectrum of the centre of the solar disk.*

The distribution of the luminosity in a refraction line depends on the values of $|n-1| = f(\lambda)$. We owe to Roschdestwensky [1]) the most accurate measurements concerning the form of this function. He found that in region of the two yellow sodium lines Sellmeier's formula:

$$n-1 = \frac{a_1\lambda^2}{\lambda^2-\lambda_1^2} + \frac{a_2\lambda^2}{\lambda^2-\lambda_2^2} + c \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

represents the observations almost exactly. We shall suppose this formula to be applicable to the cases we are considering.

If the difference between λ_1 and λ_2 is rather considerable and if we only pay attention to the surroundings of one of the lines, we may unite the latter two terms of (1) into a single, nearly constant refracting power (n_0-1), and moreover put $\lambda + \lambda_1 = 2\lambda$. The expression thus simplifies itself, if we write k for $\frac{a_1}{2}$, to:

$$n \quad 1 = \frac{k}{\lambda-\lambda_1} + (n_0-1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The intensity at any place in the spectrum depends on the *absolute* value $|n-1|$. On either side of the absorption line we mark the values of λ where $n-1 = \pm H$ (cf. Fig. 5), H being provisionally an arbitrary constant. These places in the spectrum will be called the "H-boundaries" of the dispersion line; their distance (to be

[1]) Roschdestwensky, Anomale Dispersion im Natriumdampf. Ann. d. Phys. **39**, 307, 1912.

indicated by B) is the "H-width" of the line. So B signifies the width an observer would assign to the line if he estimated its

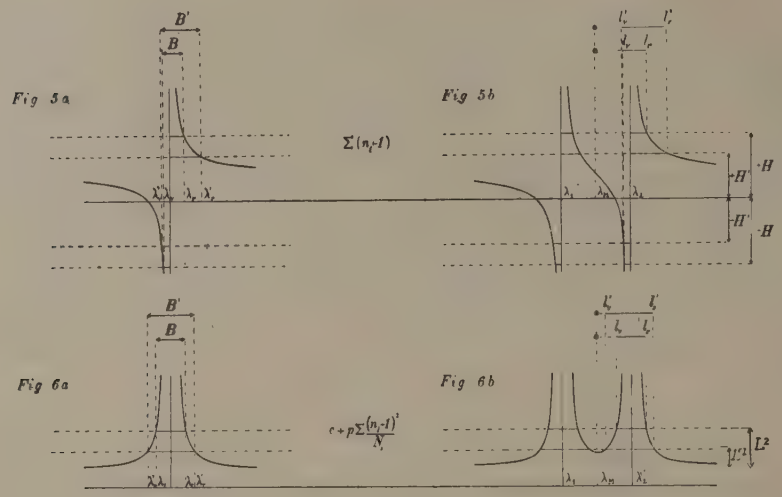

Fig. 5a–6b.

boundaries to be situated at the wave-lengths where the relative intensity has the value corresponding to H. (By "relative intensity" we understand the proportion between the intensity at the selected point of the dispersion line and the intensity in the surrounding continuous spectrum).

Suppose the "H-boundaries" of the line to be situated at λ_R and λ_V, then we obtain from equation (2);

$$\lambda_R - \lambda_1 = \frac{k}{H-(n_0-1)} \text{ and } \lambda_V - \lambda_1 = -\frac{k}{H+(n_0-1)}, \quad . \quad . \quad (3)$$

$$B = \lambda_R - \lambda_V = \frac{2Hk}{H^2-(n_0-1)^2}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or, inversely, expressing H in B,

$$H = \frac{k}{B} \pm \sqrt{\frac{k^2}{B^2} + (n_0-1)^2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We may leave the negative value of the radical out of account.

Now proceeding to the case of two neighbouring equally strong lines, we prefer to indicate the places in the spectrum by the quantity

$$l = \lambda - \lambda_M$$

(cf. Fig. 5,b) in which λ_M represents the wave-length corresponding to the point halfway between the two absorption lines, so that this

middle-point becomes the zero in our scale of l-values. If the distance between the lines is $2A$, we have in the new notation: $l_2 = A$ for the line on the red side, $l_1 = -A$ for the line on the violet side, and we get, in analogy with (2), the relation

$$n-1 = \frac{k}{l-A} + \frac{k}{l+A} + (n_0-1) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For each of the lines we may again define two "H-boundaries", to be found by taking (6) equal to $\pm H$, wherein H has the value fixed by the relation (5).

We consider the red-facing line of the pair. Its H-boundaries l_R and l_V are found by substituting in (6) H for $n-1$, l_R or l_V for l. We thus obtain, according as the $+$ sign or the $-$ sign is chosen:

$$l_R \text{ or } l_V = \frac{k}{\pm H-(n_0-1)} + \sqrt{\frac{k^2}{[\pm H-(n_0-1)]^2} + A^2} = S_R + T_R \text{ or } S_V + T_V. \quad (7)$$

Similarly it follows, that the violet-facing component of our pair has for its H-boundaries

$$l_R \text{ or } l_V = S_R - T_R \text{ or } S_V - T_V \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

§ 2. *Refraction lines in the spectrum of the limb of the solar disk.* Seen in the light of the dispersion theory, the widening of the Fraunhofer lines in the spectrum of the limb is due to the fact, that near the limb smaller values $\pm H'$ of $n-1$ are already sufficient for producing the same relative darkening, which in the central parts of the disk is only produced by the greater values $\pm H$. The H'-width, shown by the line at the limb, will be called B'. As a counterpart of (5) we now obtain the relation

$$H' = \frac{k}{B'} + \sqrt{\frac{k^2}{B'^2} + (n_0-1)^2}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and, in the case of two limb-lines, as counterparts of (7) and (7a):

$$l'_R \text{ or } l'_V = \frac{k}{\pm H'-(n_0-1)} + \sqrt{\frac{k^2}{[\pm H'-(n_0-1)]^2} + A^2} = S'_R + T''_R \text{ or } S'_V + T''_V \quad (9)$$

$$l'_R \text{ or } l'_V = S'_R - T'_R \text{ or } S'_V - T''^V \quad . \quad . \quad . \quad . \quad (9a)$$

§ 3. *Theoretical possibility of a general solution of our problem.* In principle, the formulae (5), (7), (8), and (9) embody a rather complete answer to the question how, on the basis of the dispersion

theory, the widening of the lines near the limb and the increase of their mutual influence must be connected. Indeed, if the distribution of the relative intensity were established both for an isolated refraction line of the centre type and for the corresponding limb line, it would now be possible to plot the curve giving the distribution of the light in a set of two neighbouring equal lines, and to examine how the asymmetry in it increases when passing from the centre to the limb of the disk. It would only be necessary to substitute for B and B' the values corresponding to relative intensities 0,9, 0,8, 0,7 etc., and then to calculate from (7) and (9) where the places of equal intensity ought to be found in the pair. [1])

For the present, however, the intensity curves are not sufficiently known; the observers of the solar spectrum provide us with the "visual widths" and the wave-lengths of the "centres of gravity" of the lines, quantities by no means free from subjectivity.

Nevertheless we can draw from such observations some useful inferences concerning our problem.

§ 4. *Limitation to what may be derived from already existing data.*

The average widening in the limb-spectrum of lines whose widths lie between 0,07 and 0,16 Å was found by FABRY and BUISSON [2]) to be 0,01 Å. Although we do not know the exact value of the relative intensity at the places where their interference method made them estimate the "boundaries" of the line, there was yet in this way assigned a definite width to each line. (We have some reason to think that in the ordinary visual estimates of the width of a dark line the relative intensity at the borders is about 0,8. This statement reposes on extrapolation of an empirical formula by which, in an earlier investigation, we were able to represent the visual boundaries of bright lines on the photographic plate. Cf. Ann. d. Phys., **71**, 59, 1923).

Whilst under the influence of a neighbouring line these boundaries shift asymmetrically, the central parts of the dispersion line, with

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[1]) If limb- and centre-lines have been photographed on one and the same plate (the centre spectra with shorter exposition so as to make the intensity of clear spaces equal in both centre and limbspectra) it is even possible to use the transparency values of the single lines directly for computing, by means of our formulae, the course of the transparency in pairs of lines occuring on the same plate. It is unnecessary then, first to translate the degrees of blackening into original intensities.

[2]) FABRY and BUISSON, C. R. **148**, 1741, (1909); Astroph. Journ. **31**, 97, (1910).

their greater darkness remain almost stationary. The point midway between the boundaries will, therefore, by its position depict all asymmetrical distortions of the dispersion line somewhat exaggerated in comparison with the "centre of gravity" instinctively used by the observer to identify the place of the line. If, therefore, we calculate the displacements of that *midway point*, we are sure to find *upper limits* for the displacements which, according to the dispersion theory, may be expected as the result of measurements.

§ 5. *The difference in mutual influence of refraction lines at the limb and in the centre of the disk.*

It is easily seen that the midway point M_H between the H-boundaries of the red-facing displaced refraction line is determined by the abscis

$l_M = {}^1/_2 (l_R + l_V) = {}^1/_2 (S_R + S_V + T_R + T_V)$ in the centre-spectrum,
and by (10)
$l'_M = {}^1/_2 (l'_R + l_V) = {}^1/_2 (S'_R + S'_V + T''_R + T''_V)$ in the limb-spectrum,

so that the amount of its displacement, when passing from centre to limb, is:

$$l'_M - l_M = {}^1/_2 (S'_R + S'_V - S_R - S_V + T'_R + T'_V - T_R - T_V) . \quad (11)$$

This expression contains side by side all the various systematic displacements of Fraunhofer lines which the dispersion theory foresees as consequences of irregular ray-curving. The first two terms give the general displacement of limb-lines against arc-lines; the third and fourth the general displacement of centre-lines against arc-lines [1]); the fifth and sixth term show the apparent repulsion of neighbouring lines in the limb-spectrum; the seventh and eighth the apparent repulsion in the centre-spectrum.

At present we are especially interested in the *increase* which the apparent repulsions must undergo when passing from the centre to the limb, because we are in possession of a good many observational data concerning this phenomenon [2]).

For each component of a pair the said increase is represented by:

$${}^1/_2 (T'_R + T'_V - T_R - T_V)$$

which expression, after substituting the quantities determined by (9), (8), (7) and (5), becomes

[1]) Here are, of course, not included those displacements which the core-lines or true absorption lines may perhaps be subjected to as a result of radial velocities, pressure, or fields of force. Such displacements will simply have to be added to the phenomena we are considering.

[2]) Cf.: W. H. Julius, Mutual Influence etc., Astroph. Journ. **54**, 92, 1921, and W. H. Julius and M. Minnaert, Ann. d Phys. **71**, 50, Kayser-Festheft, 1923.

$$\frac{B}{2}\left\{\sqrt{\frac{1}{\left[\frac{B}{B'}+\sqrt{\frac{B^2}{B'^2}+\frac{(n_0-1)^2B^2}{k^2}}-\frac{(n_0-1)B}{k}\right]^2}+\frac{A^2}{B^2}}+\right.$$

$$+\sqrt{\frac{1}{\left[\frac{B}{B'}+\sqrt{\frac{B^2}{B'^2}+\frac{(n_0-1)^2B^2}{k^2}}+\frac{(n_0-1)B}{k}\right]^2}+\frac{A^2}{B^2}}-$$

$$-\sqrt{\frac{1}{\left[1+\sqrt{1+\frac{(n_0-1)^2B^2}{k^2}}-\frac{(n_0-1)B}{k}\right]^2}+\frac{A^2}{B^2}}-$$

$$\left.-\sqrt{\frac{1}{\left[1+\sqrt{1+\frac{(n_0-1)^2B^2}{k^2}}+\frac{(n_0-1)B}{k}\right]^2}+\frac{A^2}{B^2}}\right\} \qquad (12)$$

In order to estimate the numerical value of this expression we base ourselves on the result of observations of FABRY and BUISSON, who found the widening at the limb to be approximately 0,010 Å with lines varying from 0,07 to 0,16 Å in width (mean width 0,11 Å). The mean width of those other lines, taken from the observational material of Mount Wilson and Kodaikanal concerning limb-centre displacements, for which the existence of mutual influence has been stated [1]) by us in the above mentioned papers, amounts to 0,09 Å. Taking these data into consideration, we have calculated the value of the expression (12) after substituting $B = 0{,}100$ Å, $B' - B = 0{,}010$ Å, and, in succession, $\frac{(n_0-1)B}{k} = \pm\infty, \pm 4, \pm 1$, and 0. The results have then been plotted as ordinates against abscisses $\frac{2A}{B}$ (which, therefore, represent distances of the lines expressed in their width as unit). We so obtained the full drawn curves of Fig. 7 (p. 346). They represent (for a refraction line) by how many thousandth parts of an Ångström unit the middle point M'_H between the boundaries of a limb-line is shifted in excess of the middle point M_H between the boundaries of the corresponding centre-line, in consequence of the presence of an equally strong neighbouring line, if this is situated at a distance equal to 3, 2, 1 times the estimated width of the lines. It will be seen that the repulsion is already perceptible at a

[1]) W. H. JULIUS, Astroph. Journ. **54**, 92, (1921); W. H. JULIUS and M. MINNAERT, Ann. d. Phys. **71**, 50, KAYSER-Festheft, 1923.

rather great distance, and increases slowly to 0,004 Å maximum. Obviously the value of n_0 has only little influence on the result.

As B' differs little from B, the radical quantities of (12) can be developed into rapidly converging series. It will then appear that as a first approximation the repulsion is proportional to the absolute value of the widening at the limb, i.e. to $B'-B$, Accordingly, our curves are also valid for lines differing in width from those here considered, provided their widening at the limb has the value found by Fabry and Buisson. They are therefore applicable to the case of lines having the average type of those for which mutual influence has been observed.

§ 6. *Diffusion-lines in the spectrum of the centre of the solar disk.* The distribution of the intensity in a pure molecular scattering line (in the absence of irregular gradients of optical density) depends on the manner in which the scattering coefficient (cf. p. 335):

$$k = C + \frac{32\pi^3}{3\lambda^4} \cdot \frac{(n_j-1)^2}{N_j}$$

varies with λ in the surrounding small part of the spectrum. And because even the variation of λ^4 may be neglected there, the distribution is entirely governed by the nature of

$$\frac{(n_j-1)^2}{N_j} = [f(\lambda)]^2,$$

a function, obviously symmetrical with respect to the position of the absorption line. On either side of the latter we may again mark a wave-length where (omitting the index j) $\frac{(n-1)^2}{N}$ equals a certain — provisionally arbitrary — quantity L^2. By these places in the spectrum we define the "L-boundaries", and by their distance the "L-width" of the diffusion line (Cf. Fig. 6, on p. 338).

We now introduce the dispersion formula (2) of p. 337 and confine our attention to the case that there is only one single absorption line, so that we may write

$$n-1 = \frac{k}{\lambda-\lambda_1} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Our two L-boundaries will be found by substituting in this equation $n-1 = \pm L\sqrt{N}$ and $\lambda = \lambda_R$ or $= \lambda_V$, which leads to

$$\lambda_R-\lambda_1 = \frac{k}{L\sqrt{N}} \quad \text{en} \quad \lambda_V-\lambda_1 = -\frac{k}{L\sqrt{N}}, \quad . \quad . \quad . \quad (14)$$

and makes the L-width of the diffusion line equal to

$$B = \lambda_R - \lambda_V = \frac{2k}{L\sqrt{N}},$$

from which follows

$$L = \frac{2k}{B\sqrt{N}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

In case we are dealing with *two* neighbouring lines of equal strength $\left(\text{that is: equal value of } \frac{k^2}{N}\right)$ at distance $2A$ from each other, it is convenient to indicate all places in the spectrum (like we did on p. 338) by a new system of abscisses:

$$l = \lambda - \lambda_M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

λ_M representing the wave-length of the point midway between the absorption lines, where we place the zero of our scale of l-values. The abscisses of the two absorption lines are now $-A$ and $+A$.

According to the equation $h = \Sigma h_i$ of p. 335, and considering the smallness of the selected spectral region, the distribution of the light in it will entirely depend on the quantity $\frac{(n_1-1)^2}{N_1} + \frac{(n_2-1)^2}{N_2}$ as a function of λ or of l. Applying (13) and (16) we find

$$\frac{(n_1-1)^2}{N_1} + \frac{(n_2-1)^2}{N_2} = \frac{k_1^2}{N_1(\lambda-\lambda_1)^2} + \frac{k_2^2}{N_2(\lambda-\lambda_2)^2} = \frac{k_1^2}{N_1(l+A)^2} + \frac{k_2^2}{N_2(l-A)^2} \quad (17)$$

The L-boundaries of each of the components of the pair are obtained by making (17) equal to L^2 or, after (15), to $\frac{4k^2}{B^2N}$. Let us consider the *red*-facing component. Its L-boundaries are situated at $l = l_R$ and $l = l_V$, and can be deduced from (17). According as the $+$ or the $-$ sign is taken, we obtain

$$l_R \text{ or } l_V = \frac{B}{2}\sqrt{1 + \frac{4A^2}{B^2} \pm \sqrt{16\frac{A^2}{B^2} + 1}} \quad . \quad . \quad . \quad (18)$$

The two *negative* values of the same radical quantities represent l_R and l_V of the *violet*-facing component of the pair.

§ 7. *Diffusion lines in the spectrum of the limb of the solar disk.* At the limb a smaller value L'^2 of $\frac{(n-1)^2}{N}$ will suffice to bring about the same degree of darkening that L^2 gave in the centre. The "L'-boundaries" determine a width B' through the relation $L' = \frac{2k}{B'\sqrt{N}}$, in analogy with (15). We thus find for the borders

of the components of our pair of limb-lines

$$l'_R \text{ or } l'_V = \frac{B'}{2}\sqrt{1+\frac{4A^2}{B'^2}} \pm \sqrt{16\frac{A^2}{B'^2}+1} \quad . \quad . \quad (19)$$

§ 8. *The difference in mutual influence of diffusion lines at the limb and in the centre of the disk.*

In conformity with our procedure with the refraction lines, we are now going to determine also in the case of pure diffusion lines an upper limit for the apparent displacements which the components of a pair impart to each other. We therefore consider the point M_L midway between the L-boundaries of one of the lines, defined by the abscis

$$l_M = {}^1/_2 (l_R + l_V)$$

and will only have to compute how much this value differs from $\pm A$. But we are especially interested in the *difference* between the apparent displacements of a component in the limb-spectrum and of the same line in the centre-spectrum, i.e. in the quantity

$$l'_M - l_M = {}^1/_2 (l'_R + l'_V - l_R - l_V).$$

for which we find, after substituting (18) and (19),

$$\left.\begin{aligned} l'_M - l_M = \frac{B}{4}\Bigg\{ & \sqrt{\frac{B'^2}{B^2}+4\frac{A^2}{B^2}} + \frac{B'}{B}\sqrt{16\frac{A^2}{B^2}+\frac{B'^2}{B^2}} + \\ & + \sqrt{\frac{B'^2}{B^2}+4\frac{A^2}{B^2}} - \frac{B'}{B}\sqrt{16\frac{A^2}{B^2}+\frac{B'^2}{B^2}} - \\ & - \sqrt{1+4\frac{A^2}{B^2}} + \sqrt{16\frac{A^2}{B^2}+1} - \\ & - \sqrt{1+4\frac{A^2}{B^2}} - \sqrt{16\frac{A^2}{B^2}+1}\Bigg\} \end{aligned}\right\} \quad (20)$$

The numerical value of this expression has been calculated for four different widths of the lines, namely $B = 0{,}050$, $0{,}070$, $0{,}100$ and $0{,}200$ Å. We took B' always to be $= B + 0{,}010$ Å, and selected a number of distances A so as to have values of $\frac{2A}{B}$ (as abscisses) suitably situated for plotting curves.

The dotted curves in Fig. 7 show the result. All ordinates should be imagined *negative*, because in this case there proves to be an apparent *attraction* of the components. We notice that the effect is

less than 0,001 Å so long as the distance exceeds twice the width of a line. On closer approach the lines rapidly grow very asym-

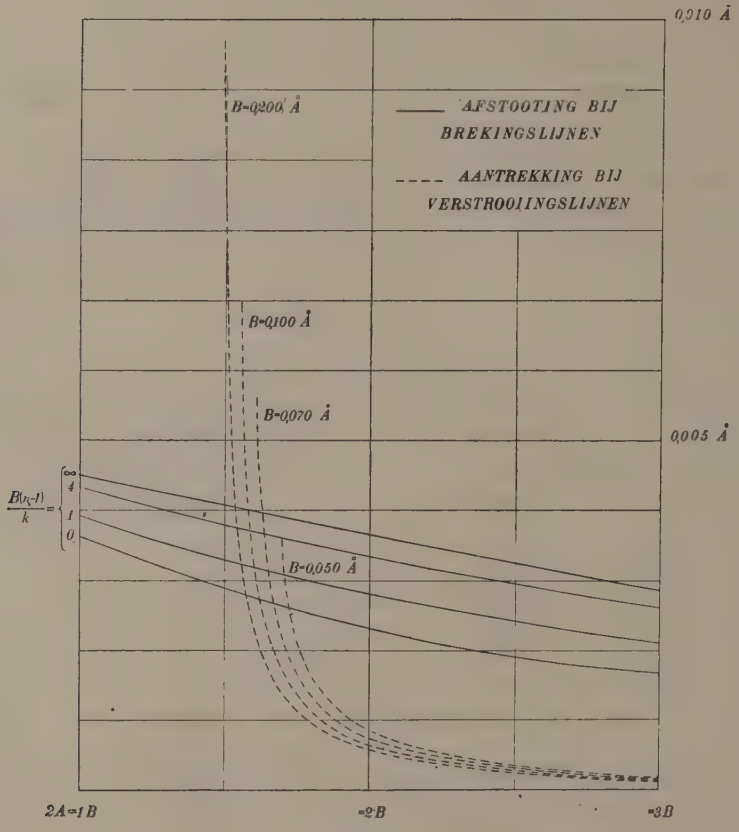

Fig. 7.

metric; at distances smaller than about 1,5 times the width, the second term of (20) becomes imaginary and the formula impracticable.

§ 9. *Comparison of the theory with the results of observations on Fraunhofer lines.*

In the foregoing we have supposed, for simplicity's sake, that the width of the true absorption lines could be neglected; but there are, of course, reasons for assigning a finite width to these cores of the Fraunhofer lines. Especially as far as very strong lines of the solar spectrum are concerned (which were not considered in the above), it would have been necessary, therefore, to base the calculations on a still closer approximation to the shape of the

dispersion curve. There is still another reason why strong lines — many of which lose their "wings" near the limb — require separate treatment, namely because for such lines, according as the limb is approached, it is indispensable to make due allowance for the spherical shape of the source of light when the consequences of diffusion, and particularly of irregular ray-curving, are inquired into. Indeed, looking almost tangentially towards the source, we are no longer allowed to assume that the darkness of the line increases with $\frac{a^2}{l}$ and with h, particularly not if n—1 has great values. Such considerations suggest that in a further development of the theory it will be necessary to reckon with a different set of conditions and circumstances for different lines, especially very near the limb, where the Fraunhofer spectrum passes gradually into the chromospheric spectrum.

The sharply differentiated structure visible in the chromosphere at times of excellent seeing indicates that, at least at a level only slightly outside the apparent edge of the disk, the gaseous medium must be highly transparent along the path of the nearly tangential rays, even for waves belonging to the very Fraunhofer lines. This proves that in those layers molecular scattering is unable to make the medium appear "foggy", in other words: that anomalous irregular refraction plays a greater part there in determining the distribution of the light, than anomalous molecular scattering.

We infer that probably with most Fraunhofer lines, also with the weaker ones, the darkness will depend to a greater extent on refraction than on molecular scattering — though it appears possible that the proportion between the respective influences differs from line to line.

All this has to be taken in consideration when comparing our theoretical results with observational data. Fig. 7 shows the upper limits of the effects of mutual influence to be expected in the cases we discussed, if the lines were *pure* refraction- or pure diffusion-lines. In Fraunhofer lines the two processes are probably intermingled and the respective displacements opposed; but refraction is likely to have the advantage.

We therefore may expect, e.g., if the distance between certain Fraunhofer lines lies between 1,5 and 3 times their width, that their mutual repulsion at the limb will exceed their repulsion in the centre by an amount certainly not greater than 0,002 Å.

Now, according to the above-mentioned observations of Mount Wilson and Kokaikanal, the examined effect has the average value

0,0017[5] Å, for pairs of lines whose average distance amounts to 1,7 times their mean width.[1]) This harmonizes, as regards order of magnitude, with the computed value.

In the publication just referred to we have shown that the mutual repulsions which two equal, symmetrical lines seem to exercise on each other as a mere consequence of systematic (photographical or psychological) errors of measurement, only become appreciable when the distance between the lines sinks below 1,5 times their width, and that, therefore, only a fraction of the mutual influence observed with Fraunhofer lines, can be ascribed to such errors.

The theoretical anticipation here advanced thus proves to be consistent with the observational material till now available; but for the present our conclusion cannot go beyond this, because the quantities involved in this investigation are near the limit of precision attainable with existing means for measurement in the solar spectrum.

Utrecht, April 1923. *Heliophysical Institute.*

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[1]) Cf. our article „Kritjsches zu Deutungen des Sonnenspektrums", Ann. d. Phys. **71**, p. 50, 1923.

Botany. — "*Cytological investigations on Apogamy in some elementary species of Erophila verna*". By J. P. BANNIER. (Communicated by Prof. F. A. F. C. WENT).

(Communicated at the meeting of March 24, 1923).

After JORDAN, in 1823 [1]), made his well-known communications concerning the constancy of the elementary species, and in particular those of *Erophila verna*, this highly polymorphic species became not merely the classic type of absolute constancy of the elementary species, but also the subject of much experimental research. The best known work on this subject is that of ROSEN on the formation of new sub-species by cross-fertilization. According to this writer the hybrids do not conform to the laws of MENDEL, but, after having formed a very heterogeneous F_2 remain constant in the F_3 and following generations [2]). The explanation of this can only be found by cytological research, accompanied by repeated efforts at hybridization.

The investigations, the principal results of which so far obtained are given here below, were prompted by similar attempts at hybridization, carried out by Dr. J. P. LOTSY between two elementary species found near Bennebroek, and further cultivated constant by him, which, as they could not be identified with absolute certainty with any previously described sub-species, were christened *Erophila cochleoides* and *Erophila violaceo-petiolata*. These experiments, however, were unsuccessful in so far as no hybrids resulted from a cross-fertilization, but all the offspring were like the mother plant, and remained constant in following generations.

One plant only, at first regarded as a hybrid, was a very fine intermediary between the two aforesaid sub-species, but further cytological examination proved that it could not be a hybrid result of the applied cross-fertilization. The following generations of this

[1]) ALEXIS JORDAN. Remarques sur le fait de l'existence en société, à l'état sauvage, des espèces végétales affines et sur autres faits relatifs à la question de l'espèce. Bull. Ass. franc. Avanc. des Sciences Lyon 1873.

[2]) FELIX ROSEN. Die Entstehung der elementaren Arten von Erophila verna. Beitr. z. Biol. d. Pfl. 1911. Bnd. X. p. 379—421.

plant were perfectly constant. They all possessed quite the habitus of the intermediary form. That the plant in question cannot be a true hybrid, but had probably arisen from a seed of another elementary species which cannot be discussed here, was however, only demonstrated with certainty by the examination of the generative nuclei.

My thanks are due to Dr. Lotsy who, in the spring of 1921, gave me part of his material for the purpose of repeating the experiment of cross-fertilization, further cultivation of the plants, and cytological examination to ascertain the cause of the constancy.

My own experiments in cross-fertilization also yielded only plants which were the same as the mother plant. The cultures of *E. cochleoides* and of *E. violaceo-petiolata*, as well as those of the intermediate form which was first taken to be a hybrid, but which, since it appears that this is not the case, I will now term *Erophila confertifolia* on account of its extremely close roset of leaves, remained perfectly constant in the years 1922 and 1923 [1]). The results of the attempts at cross-fertilization soon suggested to Dr. Lotsy the possibility of apomixy. This would not agree with the results obtained by Rosen, but if correct it might explain why his *Erophila's* remained constant in the F_2.

The following notes upon the results I obtained will prove that the supposition of apomixy was correct and that apogamy [2]) played a part in the affair.

As regards the methods, it must be remarked that the best preparations were obtained by fixing with chloroform-alcohol-acetic acid after Carnoy. The sections, after being imbedded into paraffin, were made with a Reinhold-Giltay microtome to a thickness of 5 μ. The colouring was done with Heidenhain's haematoxylin.

Like all elementary *Erophila* species hitherto described, which were found together at the same place, the sub-species here treated exhibit, besides points of great difference, also a great similarity, which a very close systematic relation suggests. *E. cochleoides* is the smallest of the three, possesses short spatulate leaves, slightly narrower towards the base and only in the older stadia showing a shallow denticulation. The stalks are strong but not of great length. On the other hand *E. confertifolia* possesses longer and softer stalks

[1]) Although the plants have not yet flowered, the constancy can be proved with a fair degree of constancy from the young rosets.

[2]) „Apogamy" is employed here in the definition of Strasburger, i. e. development of an unfertilazed diploide ovule; according to Winkler this is a question of somatic parthenogenesis.

and its very close roset has larger leaves with a fairly broad base and which exhibit several deep dentata, while in *E. violaceo-petiolata* all three characteristics are much more pronounced. Also the flower differs in form in the three subspecies.

The cytological examination in the first place brought to light that the nuclei are extremely small; in young cells in rest they are but $2\frac{1}{2}$—$3\frac{1}{2}$ μ.

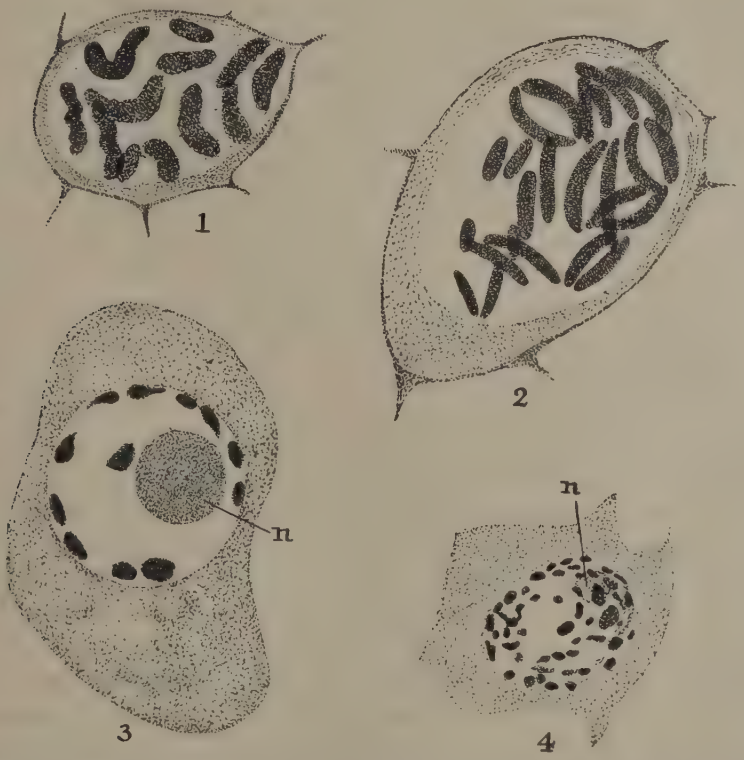

Fig. 1—4. 1 Vegetative equatorial-plate before the division of *Erophila cochleoides*. 2 Idem of *E. confertifolia*. 3 Vegetative prophase of *E. violacea-petiolata*; 4 Segmentation of the chromosomes in a vegetative cell of *E. violaceo-petiolata* *n.* = nucleolus (in all the figures). Magnification 1-2-3: 2200×; id. 4: 1100×.

Vegetative cell-divisions were studied in stem-tips, of which a cross-section is usually found in the sections through the entire inflorescence. No abnormalities are seen in the vegetative divisions of *E. cochleoides* and of *E. confertifolia*. *E. cochleoides* possesses 12 (Fig. 1), *E. confertifolia* 24 chromosomes (Fig. 2). They lie typically in pairs, a feature which recurs in all the divisions and in

nearly all the stages studied. The chromosome pairs differ appreciably in size. The vegetative cells of *E. violaceo-petiolata* exhibit a peculiarity which seems to belong only to this subspecies and occurs but very rarely in the vegetable kingdom. The normal number of chromosomes (diploid) is here 12 (Fig. 3). This number, however, was very seldom found. In almost every case the numbers found were higher and invariably different, up to 100 and probably still higher. Only in distinctly early prophases could the number 12 be found with certainty, and in very late telophases, shortly before the period of rest commences, this number is again nearly reached. In this last stage the counting is a matter of great difficulty, as the nuclei are very small and the outline of the chromosomes indistinct. Finally there is a third stage in which the normal number occurs, namely, the stage of splitting and seperation of the chromosomes. Occasionally, however, the number 12 was clearly seen. In all other stages of division the chromosomes divide up into numerous chromatic particles (Fig. 4). The longer the time is between the division stage and the resting stage, the larger is this number. How the transition from these stages and the metaphasic division-stage is accomplished could not be investigated.

The formation of the embryosac takes place in all three elementary species mainly in the same way. One large right-angled subepidermal cell immediately becomes an embryosac-mother-cell, without first forming a tapetal-cell. The embryosac grows considerably in size and the nucleus passes through a lengthy synapsis-stage. Finally it divides into two daughter-nuclei which do not divide again directly, but round off and like normal mitotic nuclei pass over into a resting-stage. A cell-wall is formed, and for a short time the two daughter-cells lie undivided. Then only does a second division take place in the two cells. Frequently the micropylar cell degenerates during this division; in other cases this takes place with the new-formed products from it. This division of the micropylar daughter-cell very often takes place in a transverse direction, whereas that of the chalazal daughter-cell always takes about the same direction as the first division of the embryosac-mother-cell. One of the four grand-daughter- or tetrad-cells, that is situated nearest to the chalaza, increases and becomes primary embryosac-cell. The other three tetrad-cells have usually degenerated by now and meet closely over the embryosac-cell.

The development of the primary embryosac-cell to an embryosac probably takes place according to the normal plan; stages with 2 and 4 nuclei are frequently met with. The nuclei lying near the

micropyle in the latter stage form the egg-cell, synergidae and one of the polar nuclei. It was not possible to ascertain whether the division of the group lying towards the chalaza takes place in the normal way, as the antipodal cells degenerate very early, perhaps even during their formation. So much is certain, however, that one or more antipodal cells and a lower polar-nucleus are always formed, and the two polar nuclei speedily fuse together.

The formation of pollen did not exhibit any special features in the cases under examination, but very typical tetrads are formed from the pollen-mother-cells. It was immediately seen, however, that the pollengrains which were formed were largely sterile. No division of the nucleus of a pollengrain was clearly observed, and artificial cultures of pollen were unsuccessful, although a considerable quantity of pollen was usually found on the ripe stigmas. From here the pollentubes penetrated to any depth only in a very few stigmas. In one single case did the pollentube reach the cavity of the ovule. Although in this way the chance of fecundation was augmented here, the ends of the pollentubes were not found in this embryosac any more then in any of the other preparations. A male nucleus was never in a single case to be found in this embryosac; the egg-cell invariably remains lying alone and after some time begins to enlarge of itself. Finally it begins to divide, after which the first embryo- and suspensor-cells are formed. The further development of the young embryo is quite normal.

While this points to apogamy, it is only proved with absolute certainty from the behaviour of the nuclei in the embryosac-mother-cells. These commence to divide. like in so many other apogamous plants, according to the heterotypical scheme. Many synapsis- and spireme-stages are observed. Instead of real gemini of chromosomes which totally or for the greater part fuse together, merely pseudo-diakinese-pairs are observed. The chromosomes approach each other, but remain at some distance from each other. After this the division has a homoiotypical character. Fig. 5 represents a telophase-stage of the division of the embryosac-mother-cell of *E. cochleoides*. In the uppermost micropylar daughter-cell the chromosomes are present in diploid number (12). The same number can also be counted in the chalazal daughter-nucleus, though less distinctly. The knife of the microtome had touched this nucleus, so that a few ends of chromosomes are to be found in the adjoining section. The figure shows which fragments in the two cross-sections belong to each other. The telophase-stage of *E. confertifolia*, which possesses vegetatively 24 chromosomes, is a still clearer and stronger proof of the apogamy,

as is shown in Fig. 6. Here there are 24 chromosomes in both nuclei; they can be best counted in the micropylar nucleus. The fact, that the chromosomes after the division still lie so clearly in

Fig. 5—9. **5.** Daughter nuclei of the embryosac-mother-cell of *E. cochleoides*, on the left the chalazal nucleus, on the right the micropylar nucleus; a^1—a^2, c^1—c^2 etc. fragments belonging to the same chromosome. **6.** Idem of *E. confertifolia*. **7.** Endosperm nucleus of *E. violaceo-petiolata*. **8** One of the three sections through a pollen-mother-cell of *E. violaceo-petiolata*. **9.** Formation of the tetrad nuclei in a reducing-division in a pollen-mother-cell of *E. cochleoides*. Magnification **5-6-8**: 2200 ×; id. **7**: 1450 ×; id **9**: 1100 ×.

pairs, points to a very strong affinity which cannot be broken by the individual splitting.

In the division of the embryosac-mother-cell and the pollen-mother-cell of the *E. violaceo-petiolata* we have the same phenomenon again as was also seen in vegetative cells, namely the segmentation of the chromosomes. It is remarkable, however, that here the chromatic particles lie in pairs, as we find all the chromosomes in the two other subspecies in pseudo-gemini. Here too very large numbers were found; approximately 50, 64, 70 and even as high as 130 or 140 were found. Fig. 8 represents such a stadium taken from a pollen-mother-cell, which had been cut into three sections, only one of which is shown here. Nevertheless about 60 chromosome particles can be counted. As the embryosac-mother-cell has exactly the same appearance and as here too the same phenomenon is seen directly after the division, it was impossible to find a pair of daughter nuclei with the diploid number to prove apogamy. Here, however, some very distinct endosperm-divisions lend assistance. As it was established that the polar-nuclei unite with each other in this apogamous plant also, the endosperm-nuclei must possess twice as many chromosomes as the embryosac-nuclei. Thus, to demonstrate apogamy this number would have to be 24, and that this is actually the case is shown by fig. 7, which illustrates a cross-section through the middle of one spindle, looking in the direction of one of the poles. The ends of the 24 chromosomes can be clearly distinguished, while the attraction of some chromosomes by the poles can also be observed.

Whereas in the divisions of the embryosac-mother-cell there is no reduction of the number of chromosomes, even though it has passed from the heterotypic phase to the homoiotypic very shortly before the division, the reducing division in the pollen-mother-cells occurs normally. During this division no peculiarity was observed in any of the cases examined other than the segmentation above-mentioned in *E. violaceo-petiolata*. Fig. 9 represents 2 sections of the tetrad nuclei of a pollen-mother-cell of *E. cochleoides*, all of which form the reduced number of chromosomes.

As has been said, however, the great majority of the pollen-grains produced from them are sterile. But even if there be fertile ones among them, they are not productive.

Thus the most important conclusion arrived at was that apogamy occurs in these three elementary species of *Erophila*, which explains the failure of the attempts at cross-fertilization. The experiments of Rosen have shown that not all subspecies are apogamous, or at

least they are not obligatory apogamous. The constancy of his new forms in the F_2 might find their explanation in apogamy. The intermediate hybrid formation in the F_1 and the singular appearance of the F_2 on the other hand, are not explained, and in respect to this a special theory would have to be applied to explain the sudden occurrence of apogamy.

Utrecht, March 1923. *Botanical Laboratory.*

Botany. — *"On the nature and origin of the cocos-pearl"*. By Dr. F. W. T. HUNGER. (Communicated by Prof. G. VAN ITERSON JR.).

(Communicated at the meeting of March 24, 1923).

In the endosperm cavity of the seed of Cocos nucifera a local calcareous formation is sometimes found to occur, to which the name of "cocos-pearl" has been given, and which must be looked upon as a highly remarkable and very rare phenomenon [1]). Such a cocoa-pearl has usually the form of a pear, or egg, sometimes it is almost spherical and has a smooth surface, as a rule of a milky-white colour. Its chemical composition corresponds somewhat to that of the oyster-pearl, from which it differs, however, in appearance by the lack of the pearly sheen.

RUMPHIUS was the first to describe this calcareous formation as "calappites" [2]), and for more than a century after him nothing was heard of this phenomenon, till at the Meeting of the Boston Society of Natural History on the 1st. of February 1860 [3]), Mr. FRED. T. BUSH presented a specimen of this cocos-pearl for chemical and microscopical examination. The research was entrusted to Dr. BACON, who submitted his report on the subject at the Meeting of the same Society on 16th. May 1860 [4]).

In 1866 Dr. RIEDEL, Ex-Resident of Menado, reported having found a pearl in a cocoanut he opened [5]). This was the first report by an eye-witness who had actually seen this phenomenon, apart from the many stories told by natives about it.

Contrary to the statement of BUSH to the effect that cocos-pearls "are said to be found free within the cavity of the cocoa-nut", SKEAT [6]) reported in 1900 that they are "usually, if not always, found in the open eye or orifice at the base of the cocoa-nut".

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1) F. W. T. HUNGER, Cocos nucifera, 2nd Ed. pp. 243—250, Pl. LXVII (1920).

2) E. RUMPHIUS, Herbarium Amboinense, Vol. I, pp. 21—23 (1741).
Idem, D'Amboinsche Rariteitkamer, pp. 291 - 292 (1741).

3) Proceedings of the Boston Soc. of Nat. Hist., Vol. VII, pp. 229 (1861).

4) Idem, Vol. VII, pp. 290—293 (1861).

5) Nature, Vol. XXXVI, pp. 157 (1887).

6) W. W. SKEAT, Malay Magic, being an introduction to the folk-lore and popular religion on the Malay Peninsula, pp. 196 (1900).

No other data regarding this remarkable phenomenon exist, and at the present day we are still completely in the dark as to the nature and origin of such a cocos-pearl.

On my last voyage to the East Indies for purposes of study, I resolved to endeavour to find out something further about the cocos-pearl and if possible solve the problem of its formation. At the same time I realised the utter futility of going to look for cocos-pearls in the Tropics on account of their extremely rare occurrence. In proof of this it may be mentioned that on a cocoa-nut estate, where approximately 3 million nuts have been opened annually for years, no such pearl has ever been found, although stories about them have led to their existence being suspected.

I therefore directed my research to gathering as many authentic data as possible.

On one of my voyages I met a native of British India who possessed a very fine cocos-pearl. According to his own account he had seen with his own eyes this specimen inside an opened cocoa-nut which had been brought to him from Madras. He assured me solemnly that his pearl had been attached to the kernel of the cocoa-nut and exactly at the place where, in germination, the cotyledon forms a haustorium.

Later on I also met with an Arab on whose cocoa-nut plantation in South Borneo a cocoa-nut had been gathered which, on being opened, proved to contain a pearl attached to the inside of it. He had dislodged the pearl from the kernel of the nut with his own hand. In this case also the pearl had been attached at exactly the same place as in the case first-mentioned.

These two corroborative declarations of eye-witnesses, who had both seen a cocos-pearl still attached inside an opened cocoa-nut, furnished me with a preliminary guiding-thread and led me to suppose that the spot which they indicated would probably be the normal point of attachment of such a cocos-pearl.

The normal germination process of the cocoa-nut begins by an enlargement of the embryo, whereby the cotyledon commences to grow inwards to an absorbing organ (haustorium), and thereby comes to protrude outside the endosperm and into the central cavity. Simultaneously with this, the plumule grows out and, breaking through the membranous operculum of the germinating pore, it pushes its way out through the hard shell.

Proceeding from the provisional determination of the place of

attachment of the cocos-pearl, the following hypothesis could now be formed. Given that the germination, being in progress, is stopped by some cause or other, thus preventing the further development of the haustorium, it is conceivable that the haustorium in this state might become encrusted by the influence of the cocoa-nut milk, and that from this the completely petrified cocos-pearl would gradually be formed.

It was now essential to find the reason for any such check in the process of germination and the accompanying solidification of the haustorium, and I wish now to submit the following remarks on this head.

At the side where the cocoa-nut has been attached to the stalk, three thin spots so-called germinating pores, or "eyes", can be seen in the hard inner shell of the fruit. As a rule one of these holes, the so-called "porus pervius", is closed by a membrane, whereas the two other, the so-called "pori caeci", are furnished with a hard tegument. In germination, the plumule pushes its way out through the porus pervius.

By way of exception there may be, instead of three, two germinating pores, viz. one porus pervius and one porus caecus, and only very rarely will there be only a porus pervius with both pori caeci entirely absent. Nevertheless a cocoa-nut of this description can germinate in the usual way.

It is a different case, however, when there is not even a porus pervius, the base of the inner shell showing no germinating pore at all, as occurs in extremely rare cases.

Such a cocoa-nut is known in the Malay language as a "kĕlapa boeta", or "klåpå boentet" in Javanese, which signifies a "blind cocoa-nut".

As remarked above a cocoa-nut without germinating pores is a very great rarity, for which reason they are regarded by the Mahommedans as sacred. The "kĕlapa boeta" is a talisman (*tjimat*) *par excellence*, and consequently it is very difficult to obtain a specimen.

This meeting with the *kĕlapa boeta* furnished me with an instance of the way in which a normal germination is rendered impossible by nature, and I did my utmost to procure some specimens.

I finally succeeded in collecting eight unopened "blind" cocoa-nuts from the East Indian Archipelago. Two of them came from South Borneo, one from Halmaheira, one from Ceram, one from the North of New Guinea, one from South New Guinea, one from the Aröe Islands and one from the Tanimber Islands, all of which I have collected personally from these several places.

Most of the specimens were very old nuts; some, according to their owners, had been preserved for scores of years as family heirlooms.

The first four "boetas" which I opened produced nothing, but in the fifth I found a really beautiful pearl still attached to the kernel; the two next produced negative results again, and the eighth specimen I have kept unopened.

The nut which had contained the pearl, as shown in Fig. 1, had been purchased from an old native at Ritabel (Larat), one of the Tanimber Islands in the Moluccas, who informed me that it had been gathered but a short time before. This proved to have been the case, because the endosperm in it was quite normal, whereas in the other nuts the kernel was either very much dried up or had even partly become a mass of brown powder.

The pearl was attached without the least trace of a stalk, being merely embedded in the endosperm (Fig. 2), and was quite easy to remove from the kernel. It lay exactly at the base of the nut, just under the spot where the germinating pores ought to have been, and thus agreed completely with the indications as given above.

This discovery, in my opinion, warrants the inference that the cocos-pearl actually represents a calcified haustorium, which has been retained in the nut after the primary germination was checked, owing to the plumule not being able to get through the shell on account of the porus pervius being lacking. As the inner shell of the *kèlapa boeta* remains hermetically closed, the newly formed haustorium becomes encrusted under the influence of the cocoa-nut milk with calcium-salts, although it still remains unexplained why the cocos-pearl consists almost entirely of calcium carbonate, while neither the cocos-kernel nor the cocoa-nut milk contains any calcium carbonates.

The belief that a *kèlapa boeta* invariably contains a cocos-pearl was sufficiently disproved by my experience that of seven specimens only *one* such formation was found in a "blind" cocoa-nut. On the other hand, it is probable, in my opinion, that it will be principally (or exclusively?) the *kèlapa boeta* that contains the cocos-pearl.

The nature and origin of the cocos-pearl as a calcareous plant germ might botanically be considered as analogous to a phenomenon seen in human and animal pathology in the petrifaction or mummification of the embryo, and termed Lithopaedion or Lithoterion respectively.

Amsterdam, March 1923.

Fig. 1. *Kělapa boeta* Basis of a blind cocoanut, without germinating pores. $^{3}/_{5}$ nat. size.

Fig. 3.
Cocos-pearl from fig. 2.
nat. size.

Fig. 2. *Kělapa boeta* Endosperm cavity with a cocos-pearl insite. $^{3}/_{5}$ nat. size.

Botany. — „*The genus Coptosapelta* KORTH". (*Rubiaceae*). By Dr. TH. VALETON. (Communicated by Prof. J. W. MOLL).

(Communicated at the meeting of April 28, 1923).

§ 1 In my paper on *Lindeniopsis*, a new sub-genus of *Coptosapelta* KORTH. (Proceedings of the Academy of Sciences of May 30, 1908) I gave a synopsis of the few species of the genus, known at that time. At my further study of the Rubiaceae of the Malay Archipelago and of New-Guinea, I again found a number of species not described at all or not in the right genus, in consequence of which this number has increased to 11. Besides it appeared from the research, that the existing diagnosis, already revised by me, could no more be applied to all species. For this reason I want to subject the chief characteristics of the genus of systematical interest to an investigation and subsequently to summarize the species known at the present time.

§ 2. *Historical review.* The genus was constituted by KORTHALS (1851) on some fruiting branches of a liane, gathered by his colleague Dr. MÜLLER on the sandy plains near Karrau (Southern and Eastern division of Borneo). He found them to belong to a new genus in the group of the Cinchoneae DECANDOLLE, of which there are but a few genera known in the Dutch Indies.

As chief characteristics he considered the liane-like habit, the fruit splitting up in two cells, each of them splitting up again and the peltate seeds provided with a fringed wing, a combination of characteristics, not yet found in any genus. In naming the genus he apparently referred to the seeds. At least I think to recognise the words κοπτω, in the meaning of „Chopping" or „Hewing" (because of the notched wings) and πελτη shield. The significance of the connecting syllabe „sa" is not clear to me. Probably the name originally ran: *Coptospelta*, a bad word-formation. As a specific name he used „flavescens", alluding to the yellowish tint the leaves get on drying.

KORTHALS's specimen is lacking in the Dutch and Dutch-Indian Herbaria. It is not apparent either, that MIQUEL knew it (1856). It was however known to HOOKER, when describing in 1876 a second species of the same genus, *C. Griffithii* HOOK f. in Icones plantarum

tab. 1089, in which he quoted KORTHALS's original and Borneo, Sumatra and Malacca as its native places. A short description of the species was afterwards given by HOOKER in HOOK. Flora indica III (1885) especially to distinguish this species from *C. Griffithii*. A little more detailed was KING in KING and GAMBLE, Flora of the Mal. Peninsula (1903).

The species however had not escaped the attention of either WALLICH or BLUME. The former published it in 1828 mistakenly as *Stylocoryne macrophylla* (= *Webera macrophylla* ROXB.), the latter took it for a new species of the same genus and gave a brief diagnosis of it in BLUME, Bijdragen (1826), as *Stylocoryne tomentosa*, while MIQUEL gave a somewhat fuller description of the same species, gathered by ZOLLINGER in Tjikoja in Java (number and date unknown), in 1856 in Fl. Ind. bat.. as *Stylocoryne ovata* MIQUEL. A third species of this genus, in order of time of discovery, is the *Coptosapelta Hammii* (subgenus Lindeniopsis) I previously discussed. It was gathered by HAM in Billiton in 1907. At about the same time a fourth species was collected in the Philippine Islands and, by E. D. MERRIL, described as *Randia olaciformis* and classed with the right genus by ELMER in 1912 (in Philippine Leaflets). A fifth species, already gathered by H. O. FORBES in British New-Guinea in 1885—86, was described by WERNHAM in 1917 (in Journ. of Botany). He classed it however with the genus *Tarenna* GAERTN. (= *Stylocoryne* WIGHT et ARNOTT). Besides I found two Borneo species undescribed in the Herbaria at Leyden and Berlin and three of New-Guinea, while finally an eleventh species was discovered, gathered bij the army surgeon JANOWSKY at the "Geelvinkbaai" in 1910.

§ 3. *Habit.* Except the deviating species *C. Hammii*, above mentioned, a half-climbing shrub, all *Coptosapelta*-species hitherto known are lianes. To all of them the excellent description by ELMER of *C. olaciformis* (Phil. Leaflets V. p. 1856) is mainly applicable: "A looping treeclimber; stem two inches thick, very irregular, heavylooping, numerously branched toward the top and forming hanging masses; leaves coriaceous, descending, curved upon the upper deeper green surface, apex recurved; inflorescence from the longer samewhat drooping branches, *erect*.

Of the species, gathered in German New-Guinea by LEDERMANN, is twice given "Liane mit beindickem Stamm", once "Liane mit armdickem Stamm". For *C. Griffithii* from Malacca as well as for the oldest species *C. flavescens* is given "Liane", to which KING's native collector adds: "A handsome creeper, 30—50 ft. high". The

two species from Borneo first described here, were probably of a similar habit. Of JANOWSKY's species is only said: "10 Meters high"; the piece of branch or stem, about as thick as a finger, gathered by him, shows a soft whitish strongly-lobed wood-cylinder with large vessels.

§ 4. *Stem* and *buds*. The rod-shaped twigs, as occurring in the herbaria, are nearly cylindrical (only in some species e.g. *C. montana* the utmost twigs are square), the nodes swollen and provided with an annular groove. As a rule only the flowering lateral and terminal branches are gathered, consequently but a few terminal buds, all of young specimens of *C. flavescens* and *C. montana* are present. These are wanting bud scales; they are formed by the two youngest leaflets, pressed together with the flat upper-surfaces, and are enclosed by the two rather small stipules only at the base. With the young growing twigs these very young leaflets are lanceolate and they consist more than half of a broad "*Vorläuferspitze*" rounded at the tip and certainly dark-green when alive (see RACIBORSKI in Flora 1900), reminding us of *Dioscorea*-species. Where there are axillary-buds, they are but a couple of mms. long, ovate, covered with long and dense hair.

§ 5. *Indument*. All species have a coat consisting of single short appressed hairs, and long hairs lying flat but free at the top; the latter are soft, straight, colourless or rarely (in sicco) yellowish, usually thinly spread; on the young twigs and leaves, the inflorescences and generally also the petioles, they are closer together, forming a soft, thin "tomentum".

On the full-grown leaves they are almost or totally absent in *C. olaciformis*, *fuscescens* and *maluensis*, where the twigs also grow bare in course of time. *C. Griffithii*, *C. Beccarii* and a hairy type of *C. flavescens* have a soft hairy covering, consisting of long curved hairs not close together.

§ 6. *Leaves*: 1. Shape: In most species hitherto known, the almost exact elliptical shape of the lamina is characteristic for the average-leaf; i. e. a symmetry of the two halves with respect to the transverse as well as the longitudinal diameter of the leaf, apart from the frequently lengthened tip and wedge-shaped base.

HOOKER (1882) and KING (1903) refer to it in their descriptions of *C. Griffithii* and *C. flavescens*, MERRILL of *C. olaciformis*, WERNHAM of *C. hameliaeblasta*.

Of course the elliptical shape is not constant with any individual, but often passes into the ovate form or becomes oblong (in this case the symmetry is preserved), the leaf-base varies between rounded and wedge-shaped. *Young plants* of *C. flavescens* have lanceolate leaves. The few known leaves of *C. Janowskii* (a mountain-species) are likewise lanceolate and provided with a long dropping-point. *C. montana* (a mountain-species from Borneo) has on several twigs elliptical and oval leaves with rounded base, and lanceolate, acuminate leaves. *C. Hammii* (the xerophilous species above-mentioned) has the tip ending in a very short hard mucro. For the rest the leaves of all species have a clearly marked acumen, sometimes very short.

2. The consistency of the leaf of old plants and twigs is thin-leathery, the colour of the upper-surface is glossy dark-green, of the lower surface lighter green with dark-green veins, in a dry condition hard and in herbaria as a rule brittle. Of young plants (see above) they are much thinner, in sicco almost membranous (in vivo herbaceous). *C. Janowskii* (see above) has likewise thin ones. When drying the leaves always change their colour to yellow or yellow-green, more or less mixed with sepia-brown, the upper-surface is as a rule dark-brown or olive-brown 153—155 (Code des couleurs de KLINCKSIEK et VALETTE). For *C. olaciformis* 183—188 or 193, or paler 217; for *C. Hammii* 202—217, for *C. flavescens* the colour of the upper-surface frequently 114, of the lower-surface 153.

3. With respect to the diagnosis of the genus as well as the species the nervature of the leaves, though showing common characteristics for all species, is of some importance. The nervature of the leaves is penniform, and the secondary or lateral veins never start from the median nerve opposite to each other at the same level, their number being as a rule rather small, 2 or 3 or 4 on each side. In many species the secondary veins next to the tip do not start above the middle of the median nerve, so that the upper half of the leaf is mainly supplied by tertiary veins. Besides they start at unequal distances from each other and are closest to each other at the leaf-base, the *lowest two* (or sometimes one) starting *close to or even from the leaf-base*; in consequence of this they resemble triplinerved and trinerved leaves (*Ficus*, *Cinnamomum*, *Viburnum*). There often starts from the leaf-base on one or both sides a secondary vein so thin, that it may be counted among the tertiary veins and may easily be overlooked; yet it follows in its course the stronger veins. After starting from the midrib these go upward in a wide curve till close to the edge, next about parallel with the edge towards the apex. The two foremost veins

end in the apex (acrodromous veins of ETTINGHAUSEN), the next run some way between the edge and the first pair and all or most of them end in the tertiary net without uniting.

The secondary veins thus run parallel to the margin for a great length and most of the basal veins partly embrace the higher ones. A definition answering exactly to this nervature, I do not find in ETTINGHAUSEN. It forms a mixture of the common *camptodromous*, (bogenläufige) with the *acrodromous* (= spitzenläufige) nervature; the term *amplexidromous* might be applied (see e. g. the figures of *Thibaudia* species (acrodromous) in v. E.'s work, besides *Nectandra* and other *Lauraceae*). The species with larger leaves *C. flavescens*, *olaciformis*, *Beccarii* have a somewhat greater number of veins (11—12), while the basal veins sometimes curve inward and unite with the preceding: schlingenläufige (brochidodromous) nervature.

The number of secondary veins of the deviating species *C. Hammii* amounts to 12; in the rather small leaves they are more crowded and fairly equally divided over the length of the leaf, joining with a curve. This is an instance of regular brochidodromous nervature, but the leaf-base is pointed and the veins are ascendent and embrace each other upward from the base, so that the character of the genus is not quite lost. The tertiary nervature is always clearly visible and equally spread over the whole leaf; the horizontal connecting veins are usually prominent and form a delicate lattice-like reticulation. Leaf-impressions made with carbon-paper usually show only this net-work.

4. Regarded biologically the leaves of *Coptosapelta flavescens* belong according to HANSGIRG (Phyllobiology, 1903, pag. 293) to the *Myrtus-* or *Lauraceae*-type with which he also classes the *Coffea*-species together with numerous other *Rubiaceae*, among which *Crossopteryx*, an african genus closely allied to *Coptosapelta*.

According to him these types are xerophilous. They belong to the periodically dry and moist regions along the Mediterranean from Spain to Palestine and also to tropical regions with similar climatological properties. As their characteristics he gives: "Strongly cutinized epidermis, rectilinear polygonal or sometimes undulated epidermis-cells, stomata sunk, very glossy lamina usually bare, sometimes grey- or white velvety, simple, narrow and entire or round, elliptical, oval and oblong, leathery and stiff", as protection against strong insolation, excessive evaporation, adhesion of water, winter-temperature, etc. Without doubt many of these properties belong to *C. flavescens*, occurring in the secondary woods of the first zone, a. o. in bamboo-woods between 200 and 500 meters, but only on

adult old plants, the leaves of which are indeed rather like those of *Coffea arabica*. Also the tomentose leaves of *C. Beccarii* and *C. Griffithii* belong to this type. On the other hand *C. Janowskii* and *C. montana* are both mountain-plants with narrower leaves and a long dropping-point, instances of HANSGIRG's "*ficus-type of the rain-woods*". To this type the young plants of the above-mentioned species also approach, in which the xerophilous habit does not much come to the fore.

Here it is not only the danger of too strong evaporation, brought along by the succession of the monsoons, but no less the risk of the damage, caused by strong rainfall which prevails.

Among the remaining species, of which *C. maluensis* does not grow higher than 200 meters above the sea-level, while the others occur at different levels in the mountains, various transitions between HANSGIRG's *Myrtus*- and *Ficus*-type are found.

An instance of real xerophilous habit is only given bij *C. Hammii* (Lindeniopsis) which as I previously mentioned should be classed with SCHIMPER's "Hartlaub formation".

§ 7. *Stipules.* The usual shape of the stipules is that of a small triangular scale, which has often been lost with the full-grown twigs in the herbaria. At the back-side and along the edges it is covered with hairs, turned to the front, often longer than the stipule and sometimes covering it entirely. The variations in shape are usually due to differences in the ratio of width and length, which depends on the width of the node. Sometimes however they may be of use in the determination of the species. This is for instance the case with *C. flavescens* and *C. olaciformis*, which show a great resemblance on superficial contemplation of leaves and flowers and were considered identical by MERRILL.

Here, in numerous specimens examined by us, the stipules are quite sufficient to distinguish between the two species. *C. flavescens* has linear-lanceolate ones, rather abruptly passing into the broad base. They vary in length between 4 and 8 mms. and strike the eye in the herbaria because, at least in the dry specimens, the back-side is absolutely bare and the broad hairy edges show clearly. *C. olaciformis* has smaller stipules, usually only 2 mms., slightly longer than broad, in old condition hairless and swollen at the base. This description has been taken from a specimen, distributed by MERRIL himself from Luzon (Ph. pl. 396) and classified as *C. flavescens*. It is also applicable to ELMER's original specimen (see below § 11. Synonymy and relationships).

§ 8. *Inflorescence.* In all species the inflorescence consists of axillary compound cymes or corymbs, starting from the leaf-axils near the top of the twigs. At the top they are closer together and often (by the reduction of the floral leaves) are combined to large terminal decussated panicles or thyrsi. Such terminal panicles also occur in other genera of the group of Cinchoneae, viz. on *Cinchona* and *Ferdinandusa.*

In the descriptions of the genus (Hooker—Schumann—Valeton in Ic. bog.) there is wrongly spoken of "thyrsi penduli". Undoubtedly the panicles are erect in all cases (see Elmers' description above, § 3), but the ends of the long branching twigs are drooping and proper flowering-branches start sideways from these. In good herbaria it may sometimes be observed how the flowering-branches form an almost right angle with the leaf-twigs.

The extension and relative length of the axis determine the character of the inflorescences with respect to the species. First of all two types may be distinguished.

The simplest case is *C. Janowskii*, a New-Guinea-Mountain-liane, where the axilary inflorescences have been reduced to single flowers and the terminal thyrsus to a simple closed raceme. The pedicels are rather long and about midway provided with two bracts. It is highly probable that on more luxuriant branches these bracts are fertile, forming forked cymes (dichasia). *C. montana* likewise has isolated flowers (uniflorous cymes) in the axils of poor flowering-branches and at the top a raceme of 5 flowers. A more luxuriant terminal twig, consisting of 6 internodia, has in the lower axils long-stalked closed racemes, bearing 5 flowers, in the following three-flowered cymes, while the top again forms a closed raceme with linear bracts. The twig of *C. Hammii* also ends in a raceme of 5—7 flowers, but with very short internodes and pedicels, so that the flowers, provided with long corollatubes, are close together and take the shape of an umbel.

In the second type both the axillary and the terminal inflorescences are compound, and the latter have the shape of corymbi or depressed (almost umbelliform) thyrsi in consequence of the decrease of length towards the apex of the internodes and peduncles; the axillary ones too are more or less corymbiform. Especially the relative length of the peduncles of the partial inflorescences, the number and density of the flowers, the number of internodes of the terminal panicles, determine the character of these species.

C. olaciformis deviates most of the rest on account of the slight extension of the corymbi and the small number of flowers. The

axillary inflorescences are short-peduncled cymes with only 3—5 flowers, many times shorter than the leaves. The terminal thyrsi consist of but 2—3 internodes and cymes with few flowers and short peduncles, and are also shorter than the higher leaves.

In the remaining species of this second type both the axillary and the terminal inflorescences are multiflorous much branched, corymbous, with moderately long or very long stalks, while the terminal panicles may consist of 5 internodes.

§ 9. *Flower and Seed.* The *calyx* is now cup-shaped, only superficially emarginate with 4—5 very short pointed teeth, now divided into nearly free sepals down to or almost down to the base, in which case the limb is not sharply separated from the ovary; in a third more frequent case cleft to the middle or a little farther. To characterise the genus it is therefore of no value, but of great value to determine the species. For all species mention should be made of the "intestinal gland papillae", (Darmdrüsen papillen: Solereder), which are placed at the inside alternate with the lobes or teeth, and resemble those which the *Rubiaceae* always bear at the inside of the stipules and are sure to occur on their calyces more frequently than appears from literature.

The *corolla* which is contorted in aestivation, but without externally visible torsion, is trumpet-shaped and reminds us of species of *Randia* and *Tarenna*, having a quinquepartite limb and as in the case of *Randia* the relative lengths of tube and limb, though not always constant in the same individual, is when the average is considered, a means of distinguishing the species.

The following average rations were found: Tube many times as long as the lobes (*Lindenia*-type), 3—6 cms. long: *C. Hammii*. Tube twice as long as the lobes: *C. Janowskii*. Tube about the same length as the lobes or a little shorter: most of the species. Tube about half the length of the lobes: *C. Griffithii*, *C. fuscescens* and *C. lutescens*. A peculiarity is, that the tube which is usually cylindrical and equally wide along its whole length, shows a sudden inflation above the middle in two species, *C. Griffithii* and *C. Janowskii*, which for the rest are farthest apart on account of the length of the corolla tube.

The internal hairy covering of the corolla tube is also of some interest. Only in 3 species *C. Hammi*, *C. olaciformis*, *C. flavescens*, the interior of the corolla tube and the filaments are glabrous. In the other species, where the filaments are covered in front with long furry hairs directed downwards, this hairy covering continues

as projecting ridges along the inside of the tube, down to the middle or till close to the base. Between these ridges the inside is covered with soft crisp hair; the descriptions of the genus however are wrong, where they say: "*Faux barbata*" for the hairy covering of the *faux* (regarded as orifice of the tube) is lacking everywhere.

When the limb is still closed, the corolla is externally entirely covered with thick-velvety or short silky hair.

The *stamina* have thin filiform filaments, which, as already observed, are congenitally attached to the corolla-tube, forming protuding ridges; the part projecting from the corolla is short and filiform, in some species hairless, in most of them covered with furry hair in front; the anthers are very narrow lanceolate and have a linear connective, coherent with the filament near the base at the backside; the long linear anthercells diverge more or less at the base, so that the base of the anther is retuse, or arrow-shaped as with *C. flavescens*, while the tip ends in a tapering point; the backside is covered with appressed hair, except in *C. Hammii*, where also the free filaments are almost lacking. The anthers hang more or less versatile from the corolla during the flowering and are curved up or contorted.

The *pistil* is highly characteristic for this genus. The stigma is wedge-shaped or cylindrical (in *Lindeniopsis* club-shaped) *not* divided into lobes, and proportionately long. The style is straight and smooth and compressed sideways, and about as long as the corolla-tube, so that the stigma overtops the corolla far. The papillary surface I generally found covered with pollen.

The *ovary*, covered with an annular disk, is regular, bilocular as in the whole group of Cinchoneae. Around a fleshy, cylindrical axis, nearly filling the two ovary-cells, are the numerous anatropous, flat, peltate, erect, imbricate ovules.

The *fruit* is globular or more or less oblong, compressed at right angles with the septum and has in a ripe condition a though, horny or thin parchment-like envelope, surrounded by a thin dry outer-integument. In very old fruits the outerlayer crumbles down and the horny valves come quite into view; in this respect there is some analogy with *Bikkia* (Condamineae). The splitting into valves is not perfectly regular. It begins with the separation of septum and axis, (loculicide dehiscence) at the top of the capsule, but next the septum itself splits, so that 4 cocci are formed open at the top and at the sides and connected at the base. This latter splitting however may fail to occur. During the splitting the fleshy placenta shrivels up, causing the numerous seeds to get gradually loose.

The *seeds* are flat, round or oblong with the hilum about in the middle (peltate) and surrounded by a membranous fringe-like notched wing, about as broad as the seed. For the distinction of species only differences in size are to be considered (except in *Lindeniopsis* where the edge of the wing is not fringed); *C. olaciformis* and *C. maluensis* have the smallest seeds; *C. Griffithii* the largest, as far as we know.

As to the process of pollination it may only be surmised. The contorted movable projecting anthers and the long protruding stigma point at the probability of wind-pollination, but the prominent flowers scenting of elder and orange-blossom may point at a connection with insects. The possibility of self- and inter-pollination is corroborated by the great mass of flowers and by the fact that (at least in the herbarium) the anthers are already open in the buds.

§ 10. The *station*: About the character of the locality in which the various species are found we only know as follows:

C. flavescens was gathered by KORTHALS on the barren sands along the river Karrau in Borneo; by KING's collector in bamboo-woods in Malacca 100—200 metres above the sea-level, by various collectors in Western Java at the foot of the mountains, on various spots in light secondary wood.

C. maluensis at 40—100 meters above the sea-level in passable primeval forest, about 20—25 meters, high; the ground covered with foliage („Galerie wald" SCHIMPER), with occasional low wood, mostly consisting of Pandanus and low feather-leaved palms (Camp Malu); idem with many tree-ferns and bamboo and Selaginella a metre high, as undergrowth (April-flusz): LEDERMANN.

C. fuscescens in "Buschwald" changing into mountain-wood up to 1500 metres above the sea-level, few large trees, many epiphytes and moss, many glades, ground often overgrown. On steep rocky slopes (Felsspitze): LEDERMANN.

C. lutescens in dense wood on hills, about 25 metres high, rather mossy; in the underwood many dwarf-fan-palms and lianes, *Freycinetia, Araceae, Agathis, Pandanus*: LEDERMANN.

§ 11. *Relationships and synonymy.* On account of the structure of ovary and fruit *Coptasapelta* belongs to the very natural tribe of *Cinchoneae* HOOKER (Genera plant. II p. 11) among which 44 genera are reckoned. This tribe is divided into two subtribes:

I. *Eucinchoneae* with a valvate aestivation.

II. *Hillieae* with an imbricate or twisted aestivation.

To the latter tribe *Coptasapelta* belongs, which genus in Genera plant. was placed among the former, a mistake already corrected by KING and by SCHUMANN.

The latter places (Pflanzenfam. IV, 4 p. 42 and 48) *Coptasapelta* immediately beside *Crossopteryx*, an African genus, I could not examine, to which only one species or group of species belongs, living on the barren Campos of Abyssinia — till lower Guinea. On comparing the detailed description OLIVER gives of this genus, I found, that nearly all more or less important characteristics given by O. are also applicable to *Coptosapelta*; only two are lacking, viz. Stigma clavatum bilobum and tubuscorollae gracilis, limbus parvus. The important characteristic of the length of the stigma however is present. *Lindeniopsis* however has a stigma clavatum and a tubuscorollae gracilis, so that only the bilobular stigma forms an important difference. This points to a close relation between these two genera, especially between *Crossopteryx* and *Lindeniopsis*, on account of the shrubby, xerophilous habit.

The leaf-nervature of *Crossopteryx* is not fully described, but the leaves have the same shape; they are larger than with most *Coptosapelta*-species, but equal to those of *C. flavescens*. The close relationship of the two genera cannot be doubted. I could not find any striking points of similarity with other genera of the tribe of *Cinchoneae*, of which but a small number of species occur in the old world. The most characteristic peculiarity, the structure of the stigma does not occur in any other genus of this tribe.

Remarkable however is the resemblance of pistil and corolla in species of two genera, belonging to the *bacciferous Rubiaceae* with many ovules, viz. *Tarenna* GAERTN. (syn. *Stylocoryne*, syn. *Webera*), which has given rise to a peculiar synonymy.

The name *Stylocoryna*, given in 1797 by CAVANILLES to a species from the Liu-tchiu-Archipelago, is formed from the words στυλος: pillar and κορυνη: club, briefly denoting the structure of the pistil of *Coptosapelta*, as described above. HOOKER referred this species to the genus *Randia* LINN., so that the characteristic generic name was lost. In 1834 WIGHT brought it up again in the form of *Stylocoryne* (independent of *Cavanilles*?) for a plant from Ceylon new to him, viz. *St. corymbosa* WIGHT, which again showed this peculiar shape of pistil. Neither could this name be kept, as the same species had previously been diagnosed by GAERTNER (in 1788) as *Tarenna zeylanica*, wich latter name of course enjoys the preference. The first generic name however had been accepted by various authors (ROXBURGH, BLUME, a.o.) and BLUME was the first to

apply it to *Coptosapelta flavescens* KORTH, discovered by v. HASSELT and himself in Java. He called it *Stylocoryna tomentosa*, while likewise WALLICH, MIQUEL and later MERRILL and WERNHAM classed species of *Coptosapelta* either with *Stylocoryne* or with *Randia* (see above p. 2).

Whether the great similarity in floral structure between two genera, belonging to different principal divisions of the family, also points to a natural relation, is still an *open* question.

§ 12. *New description of the genus. Calyx* cup-shaped, quinquepartite, quinquelobate or quinquedentate, perennial, with axillar glands.

Corolla, contorted in the bud, trumpet-shaped, tube varying in length, outside velvety or covered with sulky hair, inside bare or provided with furry ridges descending from the filaments, between those thinvelvety, straight or inflated above the middle, throat not bearded, lobes linear-oblong, obtuse.

Stamina 5, inserted on the throat, filaments filiform, short, the front furry or bare, anthers thin, linear-lanceolate, tapering at the top, at the base twice-pointed, obtuse or arrow-shaped, near the base dorsifix, on the backside provided with two rows of hairs directed upwards (in Lindeniopsis bare).

Disc small, annular.

Ovary bilocular, style anceps, hairless, stigma entire, cylindrical or club-shaped, long, far overtopping the corolla (in one species square with hairy angles); placentas coherent to the septum, ovules numerous, ascendent, imbricate.

Capsule more or less globular or oblong, bilocular, at the top loculicide bivalvular, later on quadripartite.

Seeds small, peltate, imbricate; membranous, winged all round with fringy notched (in Lindeniopsis undulate) wing; endosperm fleshy, germ straight, root straight, directed downwards.

Lianes or *Shrubs* (*Lindeniopsis*). Twigs velvety or bare, round or more or less square. Leaves opposite, thin-leathery, elliptical, lanceolate or oval, usually tapering with a rather abrupt acumen; usually hairy on the underside. Leaf-nervature more or less acrodromous. Stipules small, interpetiolar, triangular.

Flowers small or middle-sized, white or light yellow, in axillary closed racemes or trichotomous, branched cymes, united at the twig tops to many-flowered panicles.

§ 13. *Conspectus of the Species.*

I. Subgenus *Lindeniopsis*. Shrub. Seeds with a slightly crenate and undulated wing. Calyx-lobes longer than the ovary. Corolla tube long. Anthers hairless.

1. *C. Hammii*, Val. 1909.

Leaves elliptical with short, acute, hard point; secondary veins 5—7 on each side, arcuately anastomosing (brochidodromous). *Corolla* hairless inside. Twigs sharply squared. *Stipulae* very small. Plant grey velvety all over, later on bare. *Fruit* oblong, length up to 30 mms.

Distribution. Hitherto endemic in Billiton on sandy barren soil.

II. Subgenus *Eu-Coptosapelta*. Lianes Seeds with fringed wing. Calyx-lobes not longer than the ovary. Corolla tube not more than twice as long as the lobes. Backs of the anthers covered with long hair.

2. *C. olaciformis* (Merrill), Elmer 1913. *Randia olaciformis*, Merr. 1908. *C. flavescens*, Merr. (non Korth.) 1909.

Inside of corolla tube and filaments glabrous. Corolla lobes slightly longer than the tube. Inflorescences corymbose united to panicles at the tops of the twigs; cymes short-peduncled and few flowered. Flowers very small. Stipules small, triangular, no hairy edges. Leaves elliptical or oval, shortly acuminate, smaller than 100 mm. number of secondary veins 4—5 on each side, hairless when full-grown, colour in sicco pale greenish grey or olive grey. Width of fruit at most 6 mm., broader than long, calyx consisting of free oval lobes.

Distribution. Hitherto endemic in the Philippines, in the following places: Mindanao, lake Lanao, camp. Keithly, Mrs. Clemens n. 1220, 1907 (type); Mindanao, prov. of Agusan, in mt. Urdaneta, 700 M. above sea-level Elmer n. 13355?; Luzon, San Antonio, prov. Laguna, mt. Ramos Bur. of Science, Manila, n. 396!

3. *C. flavescens*, Korth. 1851. *Stylocoryna tomentosa* Bl., Bijdr. 1826; *Stylocoryne ovata*, Miq. 1856; *Stylocoryne* (*Webera*) *macrophylla*, Wall non Roxb.; *Coptosapelta macrophylla*, K. Schum.

Inside of corolla tube and filaments glabrous. Inflorescences corymbose long-peduncled and dense flowered, united at the twig-tops to large thyrsus-shaped panicles. Leaves elliptical or oval or oblong, shortly acuminate, base as a rule broad, rounded, length 80—125 mm., number of secundary veins 4—5 on each side, colour in sicco usually olive-brown, undersurface of leaves, especially along the veins thinly covered with accumbent or crisp hair. Young twigs and inflorescences coated with dense, soft hair. Fruit obovate, sepals free, oval, erect. Stipules linear-lanceolate with broad base, hairy edges.

Distribution: Malay peninsula, Burma, Western Java, Sumatra: Palembang, (Pretorius[1]), 1837, in Herb. L B; Borneo S. E. Division, on sandy plains on the river Karrau (Korthals).

4. *C. hameliaeblasta* (Wernh.) Val. nova comb. *Tarenna hameliaeblasta*

[1]) This species being rather widely spread, differs rather in habit according to the place where it is found. For instance the specimens from the Malay peninsula (Kings collector 10384 and 10393) have stronger flowering-twigs and considerably greater leaves and flowers than the specimens from Java and Sumatra. The latter are again distinguished from the Javanese form by smaller, narrower leaves, in sicco coloured darker brown, covered with crisp hair on their undersides. Similar leaves also occur in a specimen from Malacca (Maingay, 908).

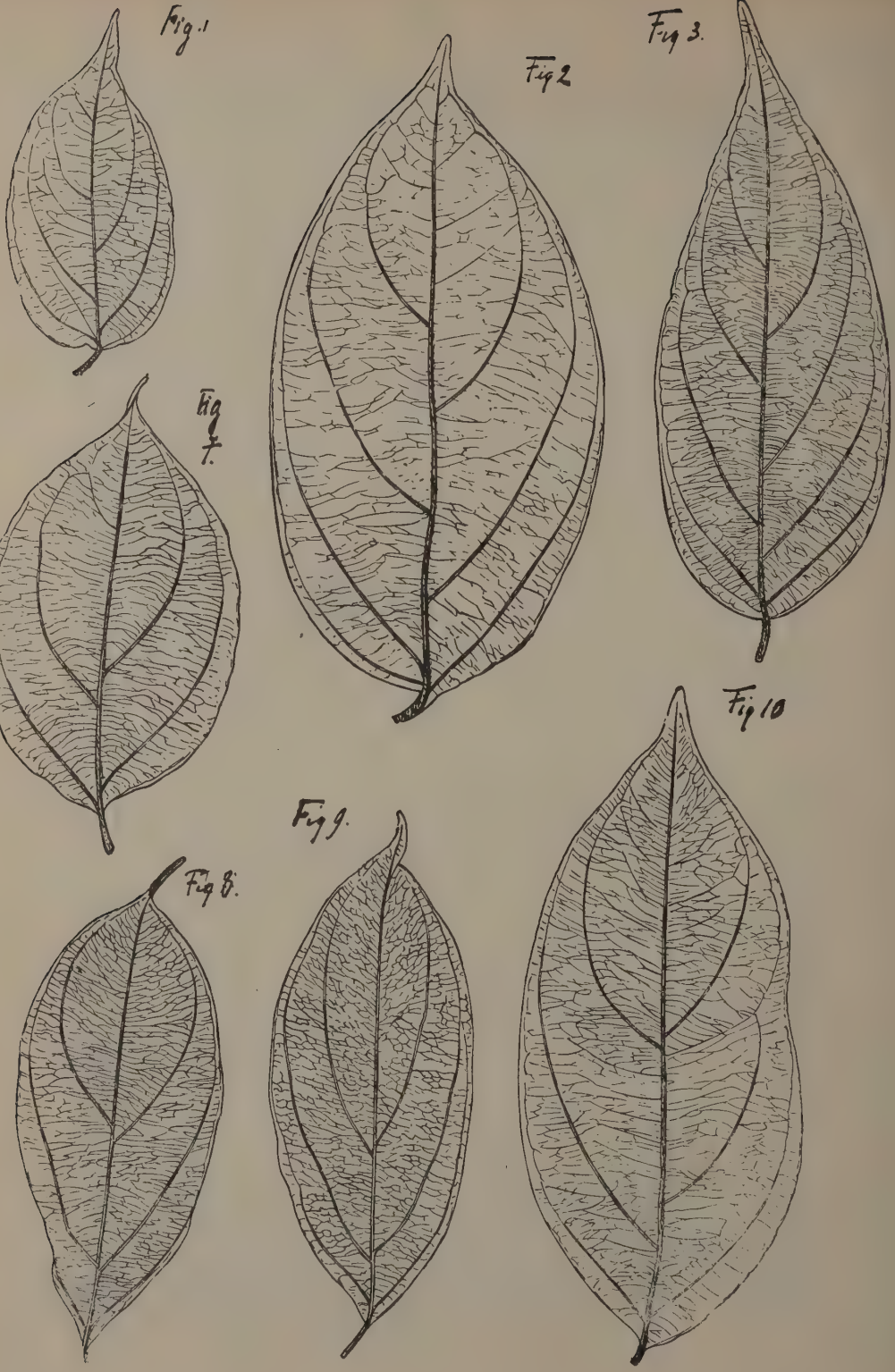


Fig. 1
Fig 2
Fig 3.
Fig 7.
Fig 10
Fig 9.
Fig 8.

Fig. 4
Fig. 5
Fig 6
Fig 12.
Fig 15
Fig 11.
Fig 13.
Fig 14.

WERNH. Inside of the upper part of the corolla tube and the filaments densely hairy, the former not inflated. Corolla lobes about as long as the thin corolla tube. Axillary cymes longpeduncled and dense-flowered; terminal thyrsi many-flowered. Corolla tube (in sicco) covered with appressed whitish hairs. Calyx lobes about as long as the ovary, erect, curved outward. Leaves oblong or elliptical, with very short acumen. Secondary veins 3—4 on each side, sometimes with an additional thin basal vein; veins erect. Stipules very small, triangular, the edges covered with dense hair. Colour of the leaves in sicco yellow-olive-green. Stalks and inflorescences hirsute, leaf-veins at the backside with remote procumbent hairs.

Distribution: British New-Guinea, Sogeri-region, 950—1400 metres above sea level. (FORBES).

5. *C maluensis*, VAL. n. sp.

Upper part of the corolla tube not inflated, hairy as are the filaments. Corolla lobes a little shorter or of equal length as the corolla tube. Axillary inflorescences with long stalks; terminal thyrsi with abundance of flowers. Flowers the smallest of the genus. Outside of corolla covered with short appressed hair. Calyx-limb divided for half its length, lobes oval, erect. Leaves usually broad, elliptical with 3—4 rarely 2 secondary veins on each side (together 5—7), acrodromous. Fruit crowned by the very small calyx-lobes. Underside of leaves with a very thin hairy covering near the edge, for the rest bare. Stipules pointed, with thin indument.

Distribution: North-East New-Guinea, at 190—200 metres above sea level, in primeval wood. (LEDERMANN).

6. *C. Beccarii*, Val n. sp.

Upper part of corolla tube not inflated and at the inside covered with long and dense hairs, as are the filaments. Corolla grey velvety externally, lobes about as long as the corolla tube. Axillary inflorescences long-peduncled, thyrsus-shaped. Terminal thyrsi with abundance of flowers. Leaves broadly oblong, ending in a caudate acumen, large, with 3—4 secondary veins on each side. Petiole fairly long; underside of leaf covered with crisp soft hair.

Distribution: Borneo (BECCARI 2271).

7. *C. fuscescens* VAL n. sp. Upper part of the corolla tube not inflated, inside covered with dense hairs, as are the filaments. Corolla lobes twice as long as the tube. Axillary cymes long-stalked and repeatedly remotely branched; terminal thyrsi many-flowered, spreading. Outside of corolla tube covered with short silky hairs, lobes hairless. Calyx small, lobes detached nearly to the base. Leaves elliptical, glabrous. Usually 3 secondary veins, or in a single specimen 2, on each side. Stipules very small, obtuse, triangular, hairy,

Distribution: Nord-East New-Guinea in mountain woods 600—1500 metres above sea level, in the Kani and Torricelli mountains (SCHLECHTER) on the Felsspitze at 1500 metres (LEDERMANN).

8. *C. lutescens*, VAL. n. sp.

Flowers as in *C. fuscescens*, but a little larger. Leaves with 2 secondary veins on each side, in sicco greenish-ochreous-yellow.

Distribution: North-East New-Guinea, on the Etappenberg at 850 m. in dense high wood (LEDERMANN).

9. *C. Griffithii*, HOOKER. f.

Upper part of corolla tube inflated, inside covered with long dense hairs, as are he filaments, lobes more than twice the length of the short wide tube. Axillary

cymes rather many flowered; terminal thyrsi densely. Outside of corolla grey velvety all over. Calyx-limb wide by cup-shaped, divided for half its length into broad lobes. Leaves elliptical, at the underside crisp hairs. Secondary veins 3—4 on each side.

Distribution. Gathered in numerous places in the Mal. peninsula, in the low lands.

10. *C. Janowskii*, VAL, n. sp.

Upper half of the corolla tube inflated, inside covered with long, dense hair, as are the filaments Corolla lobes half the length of the tube. Axillary flower-stalks with 1-3-5 flowers. Terminal inflorescences simple racemose. Flowers the largest in the genus. Outside of corolla-tube thin-velvety, lobes hairless. Calyx large, cup shaped, not incised, with short broad acute teeth. Leaves lanceolate, long-acuminate.

Distribution: Northern New-Guinea. Jabi mountains.

11. *C. montana*, KORTH. msc., in Herb. L. B.

Flowers unknown. Fruits in the leaf axils isolated or in peduncled cymes of 3-5-flowers, forming simple closed racemes at the twig-tops.

Calyx-lobes persistent on the fruit, only connected at the base, linear-subulate. Leaves lanceolate or elliptical, rather firm, with long tapering points and acute, obtuse or rounded base. Secondary veins 2-3 on each side. Stipules small, triangular, having long hairs. Stems, inflorescences and under sides of leaf-nerves thin-velvety, in sicco ochreous yellow. Fruit obovate oblong.

Distribution. S.E. Borneo. Summit of the Sakoembang, 1000 metres above sea level.

EXPLANATION OF THE FIGURES.

Fig. 1 Coptosapelta montana; Leaf of an old plant.
Fig. 2 „ flavescens, flowering plant.
Fig. 3 „ „ very young plant.
Fig. 4 „ montana; young fruiting plant.
Fig. 5 „ hameliaeblasta.
Fig. 6 „ olaciformis.
Fig. 7 = Fig. 1.
Fig. 8 and Fig. 9 Coptosapelta fuscescens.
Fig. 10 „ flavescens, flowering plant
Fig. 11 = Fig. 6.
Fig. 12 „ lutescens.
Fig. 13 and Fig. 14 „ maluensis.
Fig. 15 „ Hammii.

The figures have been obtained by carbon-impressions according to the method of ELMER D. MERRILL. Fig. 4 is not retouched, only retraced with ink.

The others have all been worked up by the designer with the aid of the original print and of the leaf; the tertiary vein system is consequently a little too prominent!

Botany. — „*Dark growth-responses*". By D. Tollenaar. (Communicated by Prof. A. H. Blaauw).

(Communicated at the meeting of April 28, 1923).

In our previous report on the light- and dark-adaptation of *Phycomyces nitens* (Proc. Vol. XXIV Nos. 1, 2 and 3, 1921) the existence of the so-called „dark-growth-response" was already proved in a great number of experiments. By dark-growth-response we understand the occurrence of a growth-response, when a sporangiophore of *Phycomyces nitens* adapted to light (by a four-sided illumination for hours at a stretch) is placed in the dark. It seemed worth while considering in how far this dark-growth-response of *Phycomyces-nitens* (the negative after-images of the human eye probably being in reality comparable) occurs in other organs.

In this communication the results are mentioned concerning the dark-growth-responses of the sporangiophore of *Phycomyces nitens*, the hypocotyledons of *Helianthus globosus*, the coleoptiles of *Avena sativa*, the roots of *Avena sativa* and the roots of *Sinapis alba*.

If possible the results have been compared with the light-growth-responses hitherto known.

Method and accuracy of the results.

In all experiments the preceding illumination was four-sided; the temperature being kept constant by means of the oil-thermostat, described in „Licht- und Wachstum I". In this way the temperature could be kept constant to 0.02° C. with moderate illuminations. It should be particularly kept in view, that the growth was as a rule only considered sufficiently constant, when it did not oscillate above 10%, i. o. w. with an average rate of growth of 100 no rates higher than 105 or lower than 95 occurred. This enables us to ascertain responses of growth more than 5% above or below the average; responses of growth therefore of an acceleration or retardation of 10% we can ascertain with some certainty.

We mention this in order to give the illustrations and reviews the value due to them, which could not be judged of without the full data — which we omit here with a view to space, but all of which will appear in the "Mededeelingen der Landbouw-hoogeschool" this year.

As long as on account of insufficient constancy of the outward circumstances or through inward causes, the growth already greatly oscillates before the change in light-conditions, it may be easily understood that a response of growth due to this one factor cannot be accurately ascertained.

As responses of growth of more than 50 % are but rare, they are not demonstrable when the growth shows such variations beforehand. With the data in literature however this repeatedly occurs. We repeat, *that for our reactions we only used organs, showing as a rule no oscillations of growth greater than* 10 %.

The figures subjoined all represent the response of individuals, approaching the average type as closely as possible. Only in the case of *Phycomyces nitens* a schematical figure of the process of reaction was given.

Just as in most of the previous curves published by BLAAUW such figures, in which the reaction-type of a definite experimental series is composed, are mainly based on the so-called *cardinal points*, to be found in the reactions of all individuals. These cardinal points are:

1. the average-point of time, at which the response of growth begins;

2. the average-time, at which the reaction reaches its first climax (either maximum or minimum of growth);

3. the average-rate of growth at that moment in percents of the original rate of growth; and next again the average time, at which eventually another maximum or minimum occurs and the average-rate of growth at that moment.

Dark- and light-growth-responses of Phycomyces nitens.

The light-growth-responses are known from the results of BLAAUW, published in "Licht u. Wachstum III" (Med. d. Landb. Hoogesch. 1918) p. 108. The cardinal points for some intensities follow:

TABLE I.

Light-intensity	First response after beginning of exposure	Maximum of response		Final rate of growth
		after beginning of exposure	in % of the rate of growth in dark	
1/8 MK.	8 Min.	9½ Min.	141 %	102 %
1 „	5½ „	9 „	148 %	103 %
8 „	5½ „	8½ „	152 %	111 %
64 „	4 „	8 „	174 %	112 %

At a temperature of about 17° C. some sporangiophores adapted to exposures to 1/512, 1/64, 8 and 64 M.K., were darkened, the growth-measuring being continued. The responses of growth, consisting in a retardation of growth were very characteristic.

The cardinal points, computed from sets of 5—6 experiments are given in the subjoined table.

TABLE II.

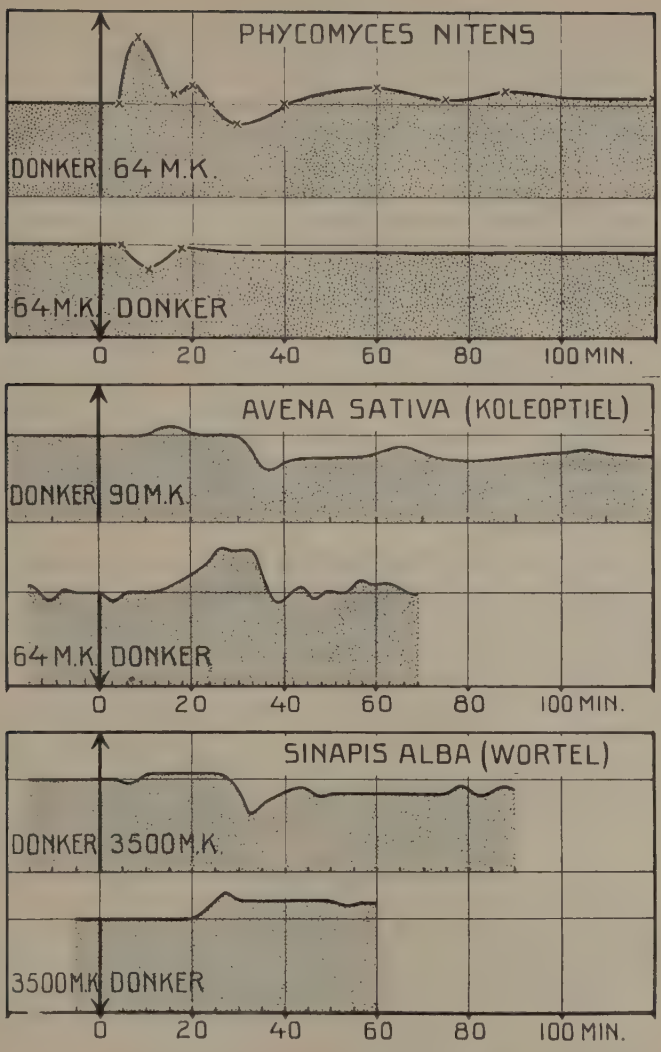
Adapted to	First response after beginning of darkening	Minimum of growth	
		after beginning of darkening	in % of the rate of growth in light
1/512 MK.	10½ Min.	12½ Min.	89 %
1/64 „	6½ „	12½ „	85 %
8 „	6 „	11 „	67 %
64 „	4½ „	10 „	73 %

The reaction at 64 MK was observed in a great number of observations (19). From the results obtained a maximum after about 17 min. could be derived with a rate of growth of about 98½% of the rate of growth in light; after that the oscillations get more and more indistinct and after 1¾—2 hours the equilibrium for the growth has externally been reached. The rate of growth appears to have become 93 % of the rate of growth in light, with a mean error of about 1 %.

From comparison of the above reports the contrary reactions, brought about by making light and dark, are clearly perceptible. (See the figure).

The dark- and light-growth-responses of hypocotyledons of Helianthus globosus.

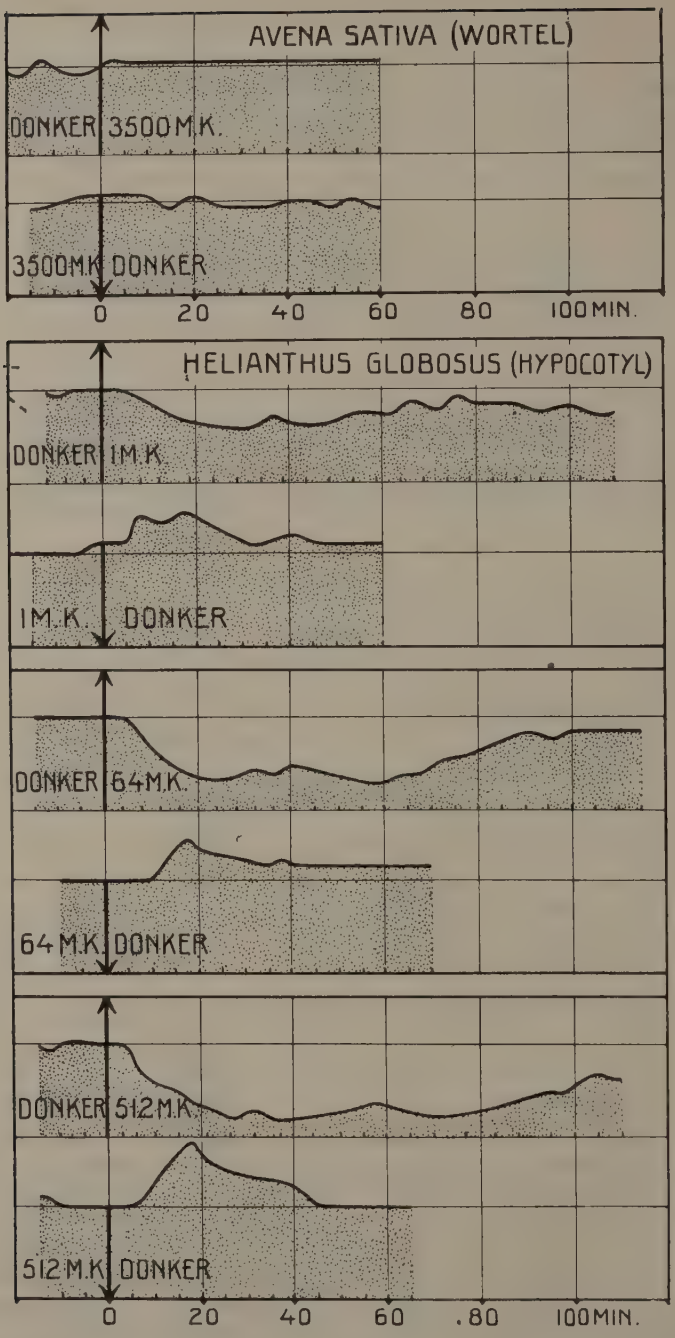
The light-growth-response of these organs is sufficiently known from "L.u.W. II". It consists in a retardation of growth, making its first influence felt, when exposed to 1 MK after 8 min.; the minimum of 74 % of the rate of growth in light appears after 27—38 minutes, after which the growth reverts to its previous rate, at least in a slight number of observations it is after 3 hours not perceptibly different from the rate before exposure.



EXPLANATION OF THE FIGURES.

These figures have been arranged in twos, in such a way, that above the process of growth has been represented when the organ after having been in dark, was permanently exposed to light (↑) below the organ made dark (↓) after having been exposed for hours. The height of the dotted space represents the rate of growth. In the case of *Phycomyces* the two growth-curves have been plotted according to the average progress of a number of individuals; the cardinal points are indicated by X For all the other organs the curves have been composed of the figures found for one of the individuals. The curve for the coleoptile of Avena sativa has been plotted after an individual reaction after KONINGSBERGER.

How these curves have been plotted will be further discussed and explained in the more detailed publication.


AVENA SATIVA (WORTEL)
DONKER 3500 M.K.
3500 M.K. DONKER
0 20 40 60 80 100 MIN.
HELIANTHUS GLOBOSUS (HYPOCOTYL)
DONKER 1 M.K.
1 M.K. DONKER
DONKER 64 M.K.
64 M.K. DONKER
DONKER 512 M.K.
512 M.K. DONKER
0 20 40 60 80 100 MIN.

At 64 MK the first reaction already appears after about 3½ min., the minimum amounting to 39 %, after 20—25 min., while after that the rate of growth gradually reverts to its initial value.

Finally at 512 MK the reaction-period is 3½ minutes, the minimum, now 21 %, appears after about half an hour and continues for a long time. Even some hours after the beginning of the exposure the rate of growth remains considerably below the rate in dark. Compare the figures subjoined.

What reaction takes place, when we darken after these hypocotyledons have been mainly adapted to a constant illumination for 5—7 hours?

The results of these experiments, made at about 20° C. have been briefly summarized in the subjoined table.

TABLE III.

Adapted to	Beginning of response after darkening	Maximum of response		Second maximum after
		After beginning of darkening	in % of the rate of growth in light	
1 MK.	7½ Min.	18½ Min.	128 %	40 Min.
64 „	8½ „	19 „	137 %	—
512 „	8½ „	18 „	157 %	—

After about an hour and a half the growth had become settled again. As to the rate, putting together all data of 1, 64 and 512 MK and comparing the rate of growth in light to the rate 1—2 hours after darkening, we find of the 14 results: a retardation of growth in 7, an acceleration in 6 and an unaltered rate in one, while an average acceleration of growth of 5 ± 21 % may be computed. Therefore the chances for the existence of a lasting acceleration of growth may be called slight.

On comparing the light- and dark-responses to each other (see figure!), we are again struck by the reverse process, though there is no perfect symmetry. In both cases the reaction is more marked for higher intensities (lower minima, resp. higher maxima).

Upon the whole the dark-response is not so strong as the light-response. The reaction-period is longer, the change in growth less intense, the external equilibrium of growth sooner restored.

The light- and dark-growth-response of coleoptiles of Avena sativa.

By means of the experiments of VOGT, SIERP and KONINGSBERGER a light-growth-response has been ascertained. On application of 90 MK on 3 sides KONINGSBERGER finds a minimum of about 55% 35—40 minutes after the beginning of the exposure — next a maximum after about 65—70 minutes (about 80 % of the rate of growth in dark) — while after 90 minutes a second minimum occurs amounting to about 65—70 % of the rate of growth in dark. The latter however continues oscillating irregularly for hours together. In the figure the curve of the light-growth-response is taken from an individual of table 9 from KONINGSBERGER's dissertation.

What reaction occurs, if we darken after the rate of growth has been in the main adapted to light for some hours?

With *Helianthus* and *Phycomyces* darkening appeared to cause less intense changes of growth, than "Light". If this should be the case with the coleoptiles of *Avena sativa*, there would be danger of this reaction finding no expression at all or but indistinctly, on account of the irregular growth of *Avena*, in consequence of occurring nutations.

We have therefore tried to eliminate or restrict these impeding movements. Not only were a great number of Oat-races observed in this respect, but also conditions of more or less moist and hot cultivation were tried. In this way we have succeeded in finding an Oat-race called "Zwarte President" which when cultivated in a very dry soil but very rarely nutates inconveniently. As long as the coleoptiles secrete little or no drops of moisture, the growth was extraordinarily constant and frequently remained within the limits fixed by us: no more than 10 % variation of growth. The temperature at which the plants grew was about 22° C. In order to give a good idea of the results, obtained for this object, we decided to give the whole of its individual responses of growth in this communication. Our preceding illumination was 4-sided with 64 MK., which intensity deviates but little from that used by the abovementioned investigators. The rate of growth has been given in microns per minute. [1])

N°. 1. Exposed beforehand for 4½ hours at 21°,9 C. to 64 MK:

[1]) The small figures denote the time of observation, by which the beginning of darkening is again put at the full hour (60).

45 $12\frac{1}{2}$ 50 $12\frac{1}{2}$ 55 $12\frac{1}{2}$ DARK! 0 $12\frac{1}{2}$ 5 $12\frac{1}{2}$ 10 $12\frac{1}{2}$ 15 $12\frac{1}{2}$ 20 13 25 **16** 30 13 35 12 40 $10\frac{1}{2}$ 45 9 50 10 55 $10\frac{1}{2}$ 1 hour $10\frac{1}{2}$ 1.05 $10\frac{1}{2}$ 1 10

N°. 2. Exposed beforehand for 4 hours at 21°,9 C. to 64 MK.
51 20 54 20 57 20 DARK! 0 19 3 19 6 19 9 20 12 19 15 18 18 18 21 **22** 24 21 27 18 30 17 33 17 38 16 41 17 44 17 47 18 50 19 53 18 56 18 1 hour 18 1.03 18 1.06.

N°. 3. Exposed beforehand for 4 hours at 22°,2 C. to 64 MK.:
51 21 54 21 57 21 DARK! 0 22 6 21 9 22 12 24 15 28 18 **29** 21 27 24 26 27 24 30 24 33 25 36 24 39 22 42 23 45 24 48 25 51 27 54 27 57 28 1 hour 26 1.03 25 1.06 25 1.09 25 1.12.

N°. 4. Exposed beforehand for 8 hours at 21°,9 C. to 64 MK.:
50 9 55 8 DARK! 0 9 5 9 10 11 15 11 20 **12** 25 11 30 $10\frac{1}{2}$ 35 10 40 $9\frac{1}{2}$ 45 10 50 10 55 $9\frac{1}{2}$ 1 hour $9\frac{1}{2}$ 1.05.

N°. 5. Exposed beforehand for 6 hours at 22°,0 C. to 64 MK.:
40 9 45 9 50 9 55 9 DARK! 0 $8\frac{1}{2}$ 5 9 10 11 15 $12\frac{1}{2}$ 20 **14** 25 12 30 **11** 35 10 40 10 45 10 50 $9\frac{1}{2}$ 55 9 1 hour 9 1.05 9 1.10 9 1.15 9 1.20.

N°. 6. Exposed beforehand for 4 hours at 21°,1 C. to 64 MK.:
45 26 48 24 51 25 54 25 57 25 DARK! 0 24 3 24 6 25 9 25 12 25 15 28 19 30 21 33 24 **36** 27 **36** 30 **36** 33 29 36 24 39 24 42 26 45 24 48 25 51 25 54 27 57 27 1 hour 26 1.03 27 1.10.

The occurring dark-growth-responses in the above cases yield the following averages for the cardinal points:

First response after beginning of darkening	Maximum of response		A minimum in the rate of growth (except in No. 5) after beginning of darkening
	After beginning of darkening	in % of the rate of growth in light	
16 Min.	± 23½ Min.	133 %	± 42 Min.

In some cases there is apparently a slight secondary maximum after 50—60 Min. (Nos. 2, 3, 4 and 6). Little may be concluded from these experiments with respect to the final rate of growth. It does not seem to deviate much from the rate in light.

The above shows a distinct response of growth, again contrary to the light-growth-response. Again it is less intense than the light-growth-response; the former gives a slighter change of growth: the undulatory movement is less vehement (undulation of shorter duration with slighter amplitude).

In the averages KONINGSBERGER's tables (4) of the light- and dark-growth-response a maximum occurring after darkening may indeed be found on pages 51, 52 and 53. It occurs after about 20—30 min., (circa 25 minutes), but also in connection with further experiments KONINGSBERGER does not consider these reactions as dark-growth-responses.

In the cases, in which VOGT observed the dark-growth-response, it lies averagely after 21—24 min., (averagely 22½ min.), which is in accordance with our results. SIERP finds his maximum averagely after 30½—35½ min. (averagely 33 min.). But we should bear in mind, that this investigator did not change the exposure to 320 M.K. to dark, but to a slighter illumination with 17.7 M.K. (pag. 699 and (following).

Accordingly in our experiments both after a previous exposure of 6 and 8 hours, and of 4 and 4½ hours, we found a dark-growth-response with the coleoptiles of *Avena*, contrary to the light-response of this organ.

The Light- and Dark-growth-responses of the root of Sinapis alba.

This organ being much less sensitive to light, I deemed it desirable to apply stronger illuminations, viz. of 3500 M.K. In spite of the insertion of a cooler with running water into the circuit, a gradual rise of temperature from 0°.5—1°.0 C. in the course of an hour could not be prevented. On darkening, a fall of temperature could be prevented by again putting the heating into operation. Then oscillations above 0°.05—0°.1 C. did not occur.

The roots were subjected to 4-sided illumination at 21°.5—22°.8 C. for 3—5 hours. First the light-growth-response was determined, yielding the following averages:

First response after	Minimum of growth		Rate of growth after some hours in light in % of the rate of growth in dark
	after making light	in % of the rate of growth in dark	
37½ Min.	39½ Min.	79 %	88 %

We observe a distinct response of growth. The retardation of growth is permanent in all cases also after the new external equilibrium of growth has been attained.

A subsequent darkening caused the following reaction:

First response after	Maximum of response		Rate of growth in dark in % of the rate of growth in light
	after darkening	in % of the rate of growth in light	
30½ Min.	35½ Min.	124 %	113 %

Here too the contrast between light- and dark-response is found. Both are fairly equally marked.

Meanwhile I have observed the dark-growth-response with an illuminating-power of 512 M.K. I found as an average of 7 experiments:

First response after	Maximum of response		Rate of growth in dark in % of the rate of growth in light
	after darkening	in % of the rate of growth in light	
27 Min.	36½ Min.	111 %	105 %

Here we already approach the limit of the reactions still perceptible, which also appeared from the fact, that a few plants *no* more gave a perceptible dark-growth-response. On subjecting these plants to an illumination of 512 M.K., there did not occur a light-growth-response either.

The sensitiveness to light, found by BLAAUW ("L. u. W. III") for Sinapis alba was greater. At the time there was even found a marked response at 64 M.K. with a minimum of 81 % and a rate of growth after 2 hours of 91 %, an equally strong response, as the one found by us for 3500 M.K. To what causes this may be owing (older seed? other Sinapis alba race?) should be further investigated into and may become an indication for the deeper cause for sensitiveness to light.

The behaviour of the tap root of Avena Sativa, with respect to light and dark.

BLAAUW did not find a perceptible response with illuminating-powers of 64—500 M.K. I exposed to 3500 M.K. Even then no reaction occurred, or so slight a reaction, that it might as well be attributed to the slight rise of temperature.

After a 3 hours exposure at a constant temperature of 20½°—22½° C. followed darkening. In not a single case there was a marked

response, i. e. the oscillations of growth remained of the size also occurring in constant circumstances (smaller than 10 %). With a reservation as to the existence of such an exceedingly slight reaction, we may observe, that the lack of a light-growth-response goes together with the lack of a dark-growth-response.

SUMMARY.

1. *With the organs observed the occurrence of a light-growth-response went together with a dark-growth-response, in the main contrary to the former.*

2. *The lack of a light-growth-response (Avena-root) goes together with the lack of a dark-growth-response. This going together seems to hold good also individually (Sinapis-root 500 MK.).*

3. *With Phycomyces, Avena coleoptile and Helianthus-hypocotyledon the dark-growth-response is less intensive than the light-growth-response: the waves have smaller amplitude and are of shorter duration so that externally a constant rate of growth is sooner attained.*

It remains to be investigated into, whether the inward equilibrium is likewise sooner restored than the externally observable light-growth-response. Equilibrium in the inward processes indeed does not coincide with the appearance of a constant rate of growth to be judged by the observer (7).

With regard to the word "dark-growth-response", used for convenience, sake, it should be borne in mind, that *dark as such does not cause the response: dark itself is not a stimulus, but the modification in energy-supply, either when suddenly occurring (light-growth-response), or suddenly ceasing (dark-growth-response), respect. increasing or decreasing.*

It may be easily understood, that stoppage of energy-supply causes a slighter and shorter reaction in an organ, i.e. it sooner settles down than when energy is supplied.

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Wageningen, April 1923.

Mathematics. — "*Representation of a Tetrahedral Complex on the Points of Space.*" By Prof. JAN DE VRIES.

(Communicated at the meeting of April 28, 1923).

1. Let there be given a pencil of quadratic surfaces which has a twisted curve ϱ^4 as base curve. The polar planes of a point P with respect to these surfaces pass through a straight line p, which we shall call the *polar line* of P. Through P there pass two bisecants of ϱ^4; the straight line p joins the points of these bisecants which are harmonically separated from P by ϱ^4. If P lies in the vertex of one of the four cones belonging to the pencil, the polar line becomes indefinite; any straight line of the plane $\omega_k \equiv O_l\, O_m\, O_n$ may be considered in this case as a polar line.

The complex of rays T of the polar lines p is represented on the space of points $\{P\}$. The side $O_k\, O_l$ is represented in any of the points of the opposite side $O_m\, O_n$. If a straight line r is to belong to T, its polar lines r' and r'' with respect to the surfaces α^2 and β^2 of the pencil, must cut each other. If the straight line r describes a plane pencil, r' and r'' describe two projective plane pencils; the plane pencil (r) contains accordingly two rays for which r' and r'' cut each other. The complex T is therefore *quadratic* [1]) and has four cardinal points O_k and four cardinal planes ω_k; hence it is *tetrahedral*.

A point P of ϱ^4 is the image of the straight line p which touches ϱ^4 at P. The scroll of the tangents of ϱ^4 is therefore represented in the points of ϱ^4.

2. If P describes a straight line r, the polar planes of P with respect to α^2 and β^2 describe two projective pencils round the polar lines r' and r''. The polar line p describes accordingly a *quadratic scroll* $(p)^2$; the conjugated scroll consists of the polar lines of r with respect to the quadratic surfaces through ϱ^4. The points of intersection of r with the cardinal planes ω_k are the images of four

[1]) If the pencil is defined by $\sum_4 a_k x_k^2 = 0$ and $\sum_4 b_k x_k^2 = 0$, the polar planes of the point y have $a_k y_k$ and $b_k y_k$ for coordinates. The coordinates of p are in this case $p_{12} = (a_3 b_4 - a_4 b_3)\, y_3\, y_4$ etc. If we put $a_1 a_3 b_2 b_4 + a_2 a_4 b_1 b_3 = c_{13,24}$, T is represented by $c_{12,34}\, p_{12}\, p_{34} + c_{23,14}\, p_{23}\, p_{14} + c_{31,24}\, p_{31}\, p_{24} = 0$.

rays p, which pass through the cardinal points O_k. T contains evidently ∞^4 scrolls $(p)^3$.

If r is a ray of T, r' and r'' cut each other, so that the projective pencils of polar planes produce a quadratic cone which has the point $r'r''$ as vertex. From this follows that the *complex cones* of T are represented by the *point ranges* (P) lying on *complex rays*.

3. The rays of T which lie in a plane φ (and which accordingly envelop the *complex conic* φ^2), are represented by the points P of a twisted curve which passes through the cardinal points O_k. For the intersection of the planes φ and ω_k is a tangent of φ^2 and is represented in O_k. As ω_k can only contain the images points O_l, O_m, O_n, the image of the system of the tangents of φ^2 is a *twisted cubic* φ^3 circumscribed to the tetrahedron $O_1 O_2 O_3 O_4$.

4. The complex T cuts a *linear complex* A in a *congruence* (2,2) which has singular points in O_k, singular planes in ω_k. For O_k is the vertex of a plane pencil belonging to both complexes, hence to (2,2). The polar lines p' and p'' of the rays of this plane pencil with respect to α^2 and β^2 form two projective plane pencils in ω_k and these produce a conic circumscribed to $O_l O_m O_n$. The *image* of the *congruence* (2,2) is therefore a *quadratic surface* Ω^2 circumscribed to $O_1 O_2 O_3 O_4$.

As A does not generally contain any of the sides $O_k O_l$, Ω^2 will not generally contain any of these sides either.[1])

The ∞^5 surfages Ω^2 are the images of ∞^5 congruences (2,2) contained in T. To these belong ∞^4 *axial* (2,2) defined by the ∞^4 *axial linear complexes*.

5. The rays of T belonging to two complexes A_1 and A_2, form a scroll $(p)^4$ of the fourth order; this scroll belongs of course at the same time to all complexes A of the pencil defined by A_1 and A_2, hence also to both axial complexes of this pencil. Their axes are director lines of $(p)^4$ and moreover double director lines, for the complex cone of a point lying on one of these axes, is cut twice by the other axis.

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[1]) If Λ is defined by $\sum_6 d_{kl} p_{kl} = 0$, Ω^2 has for equation

$$\sum_6 d_{kl} c_{mn} y_m y_n = 0.$$

Inversely the surface $\sum_6 f_{kl} y_k y_l = 0$ is the image of the (2,2), which is defined by the complex $\sum_{6} \frac{f_{kl}}{c_{kl}} p_{mn} = 0$.

The *scroll* $(p)^4$ is represented by the *twisted curve* σ^4 which is the intersection of the two surfaces Ω^2 that are the images of the congruences defined by A_1 and A_2.

If the axes r_1 and r_2 of two axial complexes cut each other, the congruence (2,2) which these complexes have in common with T, degenerates into the system of the complex rays p through the point $R \equiv r_1 r_2$ and the complex rays in the plane $\varrho \equiv r_1 r_2$. In connection with this the image surfaces Ω^2 defined by $r_1 r_2$ cut each other in the twisted curve ϱ^3 representing the complex rays in ϱ, and in the polar line r of R (the image of the complex cone of R); evidently r is one of the bisecants of ϱ^3.

If ϱ^3 is an arbitrary *twisted cubic* circumscribed to $O_1 O_2 O_3 O_4$, there pass ∞^2 surfaces Ω^2 through ϱ^3 of which any two have also in common a bisecant of ϱ^3; evidently they represent two axial complexes of which the axes cut each other, so that the corresponding (2,2) splits again up into a *complex cone* and a *complex conic*; the latter is represented by ϱ^3.

6. A *conic* $(P)^2$ has four points in common with the surface Ω^2 belonging to an axial complex A; it is accordingly the image of a *rational scroll* $(p)^4$. Any ray s of T lying in the plane of $(P)^2$, contains two points of $(P)^2$; the image S of s carries therefore two rays of $(p)^4$. Hence the curve $(S)^3$, representing the rays s, is the *double curve* of $(p)^4$.

If $(P)^2$ passes through O_1, it is the image of a cubic scroll $(p)^3$ of which the double director line passes through O_1; for the points of intersection of $(P)^4$ with ω_1 are the images of two rays p through O_1.

If $(P)^2$ passes through O_1 and through O_2, it is the image of a quadratic scroll $(p)^2$. Inversely a scroll $(p)^2$ has two rays in common with an axial complex; its image cuts accordingly the corresponding surface Ω^2 outside O_k in two points. Hence this image is either a *straight line* (§ 2) or a *conic* through two cardinal points O.

7. The points P of a plane φ represent the rays of a congruence $[p]$. The polar planes α and β of P with respect to two quadratic surfaces α^2 and β^2 of the given pencil form two projective sheaves of planes round the poles of φ. Their intersections with a plane ψ form two projective fields of rays, hence ψ contains three rays $p \equiv \alpha\beta$.

The planes α through a point Q form a pencil; one plane of the corresponding pencil (β) passes through Q, hence Q carries one ray p.

The *field of points* $[P]$ is therefore the image of a *congruence* (1,3). This consists of the chords of a *twisted cubic* σ^3 which passes through the points O; for the range of points (P) in ω_k is the image of the generatrices p of a quadratic cone which has O_k for vertex.

8. If the *twisted cubic* $(P)^3$ passes through three *cardinal points*, it is the image of a *cubic scroll* $(p)^3$. For an arbitrary surface Φ^2 representing an axial complex cuts $(P)^3$ in three more points; on the axis of this complex there rest therefore three lines of the scroll. One pencil (Φ^2) can be passed through $(P)^3$; for through any four points of $(P)^3$ ∞^1 Φ^2 can be passed, each of which contains seven points of $(P)^3$. The corresponding complexes A form also a pencil; the axes of both axial complexes belonging to this pencil, cut all rays of the scroll and are therefore the *director lines* of the *cubic scroll* $(p)^3$.

If $(P)^3$ passes through *two cardinal points*, it is the image of a *scroll* of the *fourth order*. In this case one Φ^2 passes through $(P)^3$: the scroll belongs to the congruence (2,2) which the corresponding complex A has in common with T; as it is *rational*, it has a *double cubic*.

9. A *surface* $[P]^n$ is the image of a *congruence* with *sheaf degree* n, for its intersections with a ray t of T are the images of n rays through the vertex of the complex cone represented by t. The *field degree* of the congruence is generally $3n$ for each point of intersection of $[P]^n$ with the cubic φ^3 representing the rays t lying in a plane φ, is the image of a ray of the congruence in φ. If $[P]^n$ passes s_k times through O_k, the field degree is evidently $3n - \sum_4 s_k$.

A *twisted curve* $(P)^n$ is the image of a *scroll* of the order $2n$, for the image surface $[P]^2$ of an axial complex cuts $(P)^n$ in $2n$ points, which are the images of as many rays t cutting the axis of the complex.

10. If the base of a pencil of quadratic surfaces consists of a cubic ϱ^3 and one of its chords, the polar lines of the points of space form a quadratic complex which is represented in the same way as the tetrahedral complex.

We can always represent this pencil by

$$\alpha(x_2^2 - x_1 x_3) + \beta(x_3^2 - x_2 x_4) = 0.$$

The polar planes of the point y relative to the cones $\alpha = 0$ and

$\beta = 0$ have for coordinates $y_3, -2y_2, y_1, 0$ and $0, y_4, -2y_3, y_2$. The polar line of y is therefore represented by

$$\frac{\pi_{13}}{y_3 y_4} = \frac{\pi_{23}}{4y_2 y_3 - y_1 y_4} = \frac{\pi_{31}}{2y_3^2} = \frac{\pi_{14}}{y_2 y_3} = \frac{\pi_{24}}{-2y_3^2} = \frac{\pi_{34}}{y_1 y_2}.$$

Hence

$$4p_{23}^2 = p_{13}\, p_{24}.$$

This complex has O_1 and O_4 as cardinal points, ω_2 and ω_3 as cardinal planes.

The complex cone of x touches O_1O_2 at O_1, O_4O_2 at O_4. The polar line of y lies in the plane ξ if the equation

$$\xi_1(2y_3^2 x_3 - y_1 y_2 x_3) + \xi_2 y_3 y_3 x_3 + \xi_3 y_3 y_3 x_3 + \xi_4(2y_3^2 x_3 - y_3 y_4 x_3) = 0$$

is satisfied by all values of x_2 and x_3. From this follows that the complex rays in ξ are represented by the points of the cubic which is defined by the cones

$$2\xi_1 y_3^2 + \xi_2 y_2 y_3 = \xi_4 y_3 y_4 \quad , \quad 2\xi_4 y_3^2 + \xi_3 y_2 y_3 = \xi_1 y_1 y_2.$$

(The chord O_1O_4 does not belong to the image).

The congruence (2,2) which the complex has in common with the axial complex with directrix $a_x = 0$, $b_x = 0$, has for image the quadratic surface the equation of which is

$$(a_1 b_3)\, y_1 y_3 + [4(a_1 b_4) + (a_2 b_3)]\, y_2 y_3 - (a_1 b_4)\, y_1 y_4 + (a_3 b_4)\, y_3 y_4 + \\ + 2(a_1 b_3)\, y_3^2 + 2(a_2 b_4)\, y_3^2 = 0,$$

where $(a_k b_l) = a_k b_l - a_l b_k$.

Chemistry. — "*The Electromotive Behaviour of Magnesium*". II [1]). By Prof. A. SMITS. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of March 24, 1923).

Introduction. The fact that the rest potentials of magnesium and aluminium in aqueous solutions of their salts are too small negative has been the subject of frequent comment.

An apparently succesful explanation was that which assumed the presence of a film of oxide on the metal. This was however due to a not sufficiently careful examination of the consequences of such a premise.

This is especially true in the case of aluminium where it had been supposed, that the etched or even the polished metal was coated with a not porous film of oxide of molecular thickness.

Now a number of different investigations have proved with certainty that if an etched or polished aluminium electrode is immersed in mercury above which there is an aqueous solution of the aluminium salt, the aluminium immediately shows the potential of the mercury layer, whilst there was no indication of the penetration of a film of oxide [2]).

It follows from these investigations that either a film of oxide does not hinder the passage of the electrons or there is no film at all.

If the electrons only were going through an oxide layer we should expect the behaveour of a gas electrode. This is not in accordance with the fact. Consequently if the oxide film existed it would be penetrable for ions, but it is then manifest that we are dealing with a metal-electrode.

Now it is possible that under certain circumstances the liquid in the liquid bounding layer is saturated with respect to the hydroxide of the metal. This could easily be proved by the fact, that in the formula

$$E = -\frac{0.058}{\nu} \log. \frac{L_M}{(M_L^{\nu\cdot})} - 2.8 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1]) The considerations applied here are explicated in the book "Theory of Allotropy". Longmans, Green and Co. 1922.

The first Communication appeared These Proc. Vol. XXII, 876 (1920).

[2]) See Zeitschr. f. Electr. Chem. **27**, 523 (1921) and **28** (1922).

(M_L^{ν}) can be substituted by $\frac{L_M(OH)_\nu}{(OH_L')^\nu}$ so that

$$E = -\frac{0.058}{\nu} \log. \frac{L_M(OH')^\nu}{L_M(OH)_\nu} - 2.8 \quad . \quad . \quad . \quad (2)$$

or

$$E = -\frac{0.058}{\nu} \log. \frac{L_M}{L_M(OH)_\nu} \cdot \frac{K_W^\nu}{(H_L^{\cdot})^\nu} - 2.8 \quad . \quad . \quad . \quad (3)$$

From which it appears, that the electrode will behave as an oxygen or hydrogen one, but that the electromotive forces will show a constant difference.

These considerations however are no help to us, for expression (1) which always holds good, requires the potential of the metal to be very negative, because the concentration of the metal ions in a saturated solution of $Mg(OH)_2$ or $Al(OH)_3$ is very small. The exact converse is observed.

Ten years ago KISTIAKOWSKY [1]) calculated the normal potentials neglecting the temperature coefficient in the formula of GIBBS-HELMHOLTZ and found with Mn, Fe, Co, Cu and Cd differences between the calculated and experimentally found normal potentials of 10—60 m.V.; with Ni, Sn, Pb and Hg differences of 140—190 m.V.; with Ag he found diverences of 310 m.V., and with Tl of 360 m.V., whilst the difference with Al was 460 m.V. and with Mg 900 m.V.

As KISTIAKOWSKY found the electromotive force which the calculated for Mg and Al so much higher than that found experimentally, he simply assumed that at the two electrodes in the galvanic cell metal-electrolyte-hydrogen, the reactions

$$M_S \rightarrow M_L^{\cdot\cdot} + 2\theta_L$$

and

$$2\theta_L + 2H_L^{\cdot} \rightarrow H_{2G}$$

do not take place as in other cases, but the following:

$$M_S + 2\,OH_L' \rightarrow M(OH)_{2S} + 2\,\theta$$

and

$$2\,\theta + 2\,H_2O_L \rightarrow 2\,OH_L' + H_{2G}.$$

It should be noticed that the remarkable assumption is made there,

[1]) Z. f. phys. Chem. **70**, 206 (1910).

that a reaction which takes place at the hydrogen electrode is reversed when Mg is replaced by zinc.

KISTIAKOWSKY, however, rightly comes to the following conclusion: "Hieraus fogt unmittelbar, dass die Mg bzw. Al. Electroden die Eigenschaften von Gaselektrode besitzen mussen, d.h. ihr E_h von der Metallionen-konzentration unabhängig, dafür aber von der $H^{\cdot}$ und OH'-Konzentration abhängig sein muss; ausserdem muss es, wie bei Pt, von den reduzierenden Eigenschaften des Elektrolyten abhängen."

In this KISTAKOWSKY, however, quite overlooked that the behaviour of an hydrogen electrode will also be found with any other metal, if the boundary liquid consists of a saturated solution of the metal hydroxide.

KISTIAKOWSKY, instead of measuring the Mg and H_2 potentials in the same solution by changing the Mg concentration, dipped his Mg electrode, besides in a solution of $MgSO_4$ and in a solution of $MgCl_2$, in different other solutions, not containing Mg, and then obtained results, of course, from which no conclusions at all can be drawn. In his opinion, however, his results proved that the Mg-potential is independent of the $Mg^{\cdot\cdot}$-concentration.

BECK [1]) was the first to demonstrate in his Thesis for the Doctorate the invalidity of KISTIAKOWSKY's views; he has also shown experimentally that Mg *never* behaves as a hydrogen electrode. All the same electromotive behaviour of Mg in $MgSO_4$-solutions of *slight* ($H^{\cdot}_L$) was not yet cleared up, for it appeared to him that the difference in potential between the Mg and H electrodes in these solutions of small $H^{\cdot}$-concentration increases with the Mg-concentration. [2])

BECK found that the Mg electrode does not behave as a hydrogen electrode, but the Mg does not behave as a normal metal electrode either, for it was found that the Mg-electrode becomes more negative when the $MgSO_4$-concentration increases. It further appeared that on increase of the $H^{\cdot}$-concentration the Mg-potential becomes more negative, and that it reaches a maximum negative value for every $MgSO_4$-concentration at a definite $H^{\cdot}$-concentration. This maximum negative value varied with the $MgSO_4$-concentration, at least qualitatively, in a normal way.

[1]) Rec. trav. chim. **41**, 353 (1922).

[2]) All the measurements were carried out by BECK in an atmosphere of very pure hydrogen, with vigorous stirring of the liquid, the Mg-electrode being at rest. If was found, that this way of stirring is much better than stirring by the electrode it self.

The maximum negative potentials are however no equilibrium potentials, that follows already from this, that the potential of Mg activated by amalgation in a solution of 1 gr. mol of $MgSO_4$ per litre, is more negative, i.e. — 1.856 Volt. instead of — 1.790 Volt, which value will also lie still below the real normal potential of equilibrium of Mg, as will be shown below.

Magnesium.

After this introduction we shall examine the metals Mg more closely.

The difficulties which are usually encountered in the study of the electromotive behaviour of magnesium and aluminium are owing to the fact that extraordinary phenomena appear when the usual methods of determining the equilibrium potential are applied to these strongly basic metals.

For example, suppose that the Mg potential is —1.86 Volt. Since the Mg electrode develops hydrogen, this means that the above potential corresponds to the potential of the three phase equilibrium, magnesium (inner equilibrium) — hydrogen (by inner equilibrium) and the surrounded liquid layer.

The liberation of gaseous hydrogen takes place because hydrogen ions from outside diffuse into the surrounding liquid layer and combine with the electrons.

The above assumption holds for Fe and Zn because it can be shown by calculation that the surrounding liquid layer can coexist with metal and hydrogen, the two latter in inner equilibrium.

If however we take now strongly basic metals, we can see that the quotient $\frac{(M^{\cdot\cdot})}{(2H^{\cdot})}$ would be so large, that the electrolyte would become inconsistent.

The question now arises: "Can the above negative potential (—1.86 Volt) be the potential of magnesium and unary hydrogen (that is to say hydrogen in inner equilibrium) with respect to the surrounding liquid layer containing say 1 gr. ion Mg per litre."

Applying the formula $E = -\frac{0.058}{2} \log. L_{Mg} - 2 . 8$ [1]) and substituting for E the value — 1.86 we can calculate that

$$L_{Mg} = (Mg_L)(\theta_L)^2 = 10^{2\times-16}.$$

If we consider that for hydrogen in inner equilibrium

[1]) The Theory of Allotropy p. 123.

$$L_{H_2} = (H_L^{\cdot})^2 (\theta_L)^2 = 10^{2\times -48}$$

it will be seen, that for the surrounding liquid layer which is in electromotive equilibrium with magnesium and hydrogen the following formula holds good:

$$\frac{(Mg_L^{\cdot\cdot})}{(H_L^{\cdot})^2} = \frac{L_{Mg}}{L_H} = 10^{2\times 32}.$$

It is evident that this ratio is not realizable.

If we chose $(Mg_L^{\cdot\cdot}) = 1$ then $(H_L^{\cdot})^2 = 10^{2\times 32}$ and since $(H_L^{\cdot})(OH_L') = 10^{-14}$ we have $(OH_L') = 10^{18}$.

If we take $(Mg_L^{\cdot\cdot}) = 10^{-4}$ then $(H_L^{\cdot}) = 10^{-24}$ or $(OH_L') = 10^{10}$.

From the above figures it is seen that if magnesium is in such a state that the solubility product is $10^{2\times -16}$ it can never coexist with unary hydrogen and liquid because the surrounding liquid layer, required for this coexistence, cannot exist.

A graphical representation of the above statement in E,X diagram (fig. 1), is given by the point C. C lies so near one axis that any stable aqueous solution lies to the right of it. If we assume that the

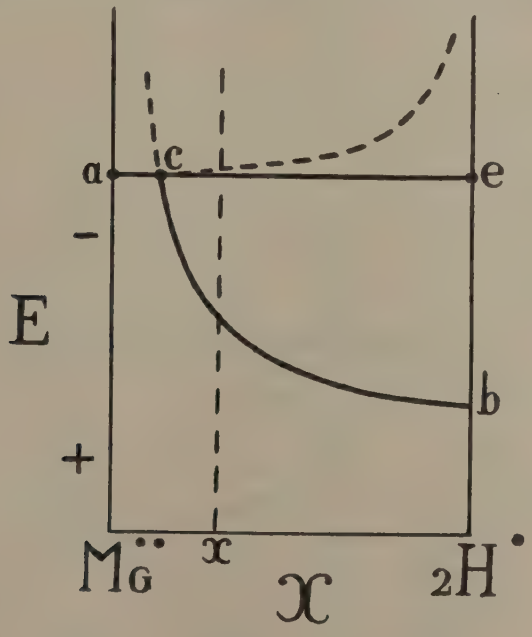

Fig. 1.

solution into which the Mg electrode is dipped has the composition X then there are two limiting possibilities for the coexistence of

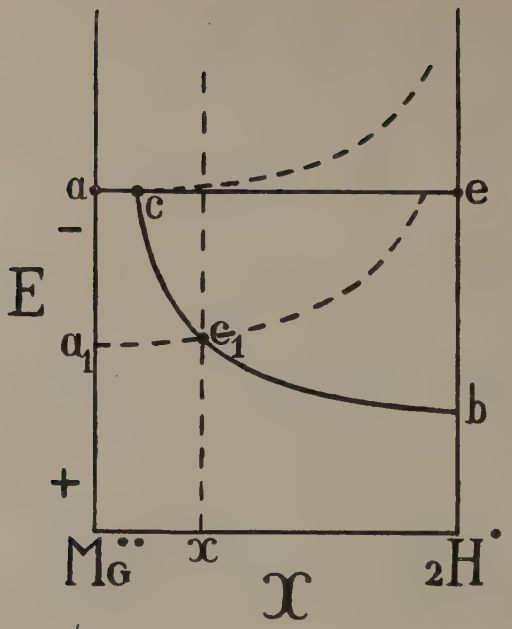
a
c
e
E
−
a_1
c_1
b
+
$M_G^{\cdot\cdot}$
x
$_2H^{\cdot}$
x

Fig. 2.

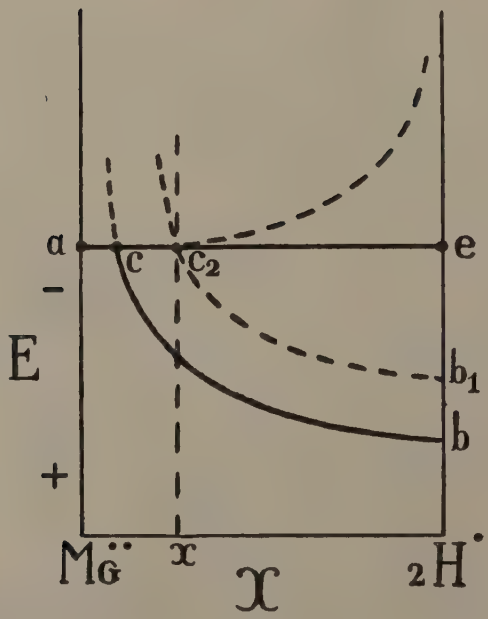
a
c
c_2
e
E
−
b_1
b
+
$M_G^{\cdot\cdot}$
x
$_2H^{\cdot}$
x

Fig. 3.

Mg, hydrogen and electrolyte. Between these limits the observable cases lie.

One limit is indicated in fig. 2. Here the hydrogen is in inner equilibrium but that of the Mg is displaced to such an extent that the potential line of this metal has the position $a_1 c_1$.

At the other limit the Mg remains in inner equilibrium but the liberating hydrogen is in a state of formation so that its potential line has the position $b_1 c_2$ in fig. 3.

In the latter case the observed potential of the three phase equilibrium $ac_2 e$ will practically correspond with the equilibrium potential of Mg [1]). The observed cases lie between these limits.

The above remarks concerning Mg with a potential of —1.86 V. also apply to Mg with a potential of —1.3 Volt. In this case $L_{Mg} = 10^{2 \times -26}$ and then $\frac{(Mg_L^{\cdot\cdot})}{(H_L^{\cdot})^2} = \frac{L_{Mg}}{L_{H_2}} = 10^{2 \times 22}$, so that if $(Mg_L^{\cdot\cdot}) = 1$, $(H^{\cdot}) = 10^{-22}$ or $(OH') = 10^{8}$.

Consequently when Mg of a potential of —1.3 V. was liberating hydrogen in inner equilibrium from a solution of a Mg salt in which $(Mg_L^{\cdot\cdot}) = 1$, then OH' in the surrounding liquid layer would be 10^8. This is practically also an impossibility.

From the above it follows that the hydrogen which coexists with magnesium and the surrounding liquid must be in such a condition that the value of L_{H_2} is much greater than that corresponding to the inner equilibrium.

This statement arouses a suspicion to the precipitations of Mg-hydroxide in the surrounding liquid layer, but if this occurred the coexisting hydroged would be formed in a stronger state of formation than even in the case that the surrounding liquid is no longer saturated with respect to $Mg(OH)_2$.

The solubility product of $Mg(OH)_2$ is about $10^{-10.5}$ since the value we choose for Mg_L is immaterial we will assume $(Mg_L^{\cdot\cdot}) = 1$. In this case $(OH_L') = 10^{-5.25}$.

If the Mg-electrode has the value $L_{Mg} = 10^{2 \times -26}$ we have already calculated that $(H_L^{\cdot}) = 10^{22}$ or $(OH_L') = 10^{8}$ which is quite impossible for the solubility product of $Mg(OH)_2$ requires here $(OH') = 10^{-5.25}$.

---

[1]) Here it must be remarked, that if hydrogen is being liberated the composition of the bounding liquid layer will always lie more to the lef than that of the liquid outside.

It is therefor evident that the apparent solubility product of hydrogen shows large deviations, from the value which would be expected when the hydrogen is in inner equilibrium. We will now calculate what the value of the solubility product of hydrogen must be in this case.

In the above we have manifestly employed a value for L_{H_2} which is $10^{2\times 13.25}$ times too small. The value of L'_{H_2} for the hydrogen which is being liberated, in the case under considerations, is therefore $10^{2\times -34.75}$ instead of $10^{3\times -46}$. In other words this hydrogen has become so much more basic, that in respect to its electromotive behaveour it somewhat resembles zinc.

If the OH-ion concentration in the surrounding liquid layer is lower than $10^{-5.25}$ then no precipitation of $Mg(OH)_2$ will take place. If $(OH'_L) = 10^{-10}$, then $L'_{H_2} = 10^{2\times -30}$ and electromotively the hydrogen is beginning to resemble manganese.

From the above considerations it follows that an approximation to the equilibrium potential of magnesium would only be possible if the hydrogen could appear in a stronger state of formation, for, as already has been demonstrated, an increase in the solubility product of magnesium will always be accompanied by an increase in the solubility product for the hydrogen which is being liberated. This is not necessary the case with less basic metals. It is clear that the foregoing conclusions will also hold for aluminium and we will now examine the conditions under which we can measure the most active potentials of these metals.

According to the theory of capillarity the change between two liquid phases or between a liquid and a gaseous phase is really an extremely sharp change in continuity. In the above case however we are dealing with random arrangements of particles in each phase. When we come to consider a metal and an electrolyte one has a definite structure and the other has not.

We are however sure, that in this case also in the bounding layer there will be a very sharp transition, though with a discontinuity, and that consequently the coexisting phases will only show quantitative differences with respect to compositions.

Now we make the assumption, that the parts, present in the metal bounding layer, in concentrations depending in the depth of the layer, in general will exert influence in the rapidity, with which the inner equilibrium is establishing in the bounding layer.

Oxygen, nitric acid, nitrates, etc., are already known to exert a retarding influence on the establishment of internal equilibrium in

metals and the electromotive behaveour of Mg and Al now shows that their oxids and hydroxides may exert a similiar influence.

In a solution of $MgSO_4$, to which no acid is added, some $Mg(OH)_2$ is in solution. If we dip a Mg-electrode into this solution then, besides other parts, present in the electrolyte, also $Mg(OH)_2$ will solve in the metal bounding layer. This does not mean to say, that the Mg will lose any of its characteristic properties such as the power to precipitate mercury from a solution but this small quantity of $Mg(OH)_2$ seems to exert a retarding influence on the velocity with which the internal metallic equilibrium is established.

A Mg-electrode under the above conditions dissolves slowly, evoluting hydrogen, and shows too low a potential owing to the disturbance of the inner equilibrium. Addition of sulphuric acid however decreases hydrolysis, and with this the $Mg(OH)_2$ concentration in the metallic surface and induces a change in the direction of the inner equilibrium of the metal, such that the potential becomes more strongly negative.

This effect of adding acid is however twofold. On the one hand the concentration of the negative catalyst in the metal $Mg(OH)_2$ is decreased, on the other hand direct attack at the metal is increased. This attack in cases where it is rapid, such as the one under considerations, always gives rise to disturbances and it might be expected, that the potential would first become more negative and finally would fall a little.

This was found to be the case by the author and the Gruyter and also by Beck.

Beck's table XII p. 42 shows this quite plainly.

This table shows in addition that the differences between the Mg and the hydrogen potentials are not constant and that, whilst the hydrogen potential is becoming decreasingly negative, the magnesium potential changes in the opposite direction.

This means that Mg does not behave as a hydrogen electrode, which would be the case if the magnesium surface was unchanged and moreover was surrounded by a liquid layer saturated with respect to the $Mg(OH)_2$.

It is probable that this was the case with some solutions when the H-ion concentration was very low, merely with the vigorous stirring employed in these experiments. The certain conclusion from Beck's experiments is that, whether the surrounding liquid layer was saturated with respect to $Mg(OH)_2$ or not, the state of the Mg bounding layer was changing with the hydrogen concentration.

By increasing the hydrogen concentration the magnesium bounding

layer became more basic that is to say the normal inner equilibrium tended to be established.

Another phenomenon showed by Beck which has not yet been considered is that the potential of Mg in $MgSO_4$ solutions alone becomes more negative as the concentration increases.

Up to the present it has always been observed that a metal dipped into dilute solutions of the corresponding sulphates or chlorides were more early disturbed than in concentrated solutions of the same salts. This was particularly the case with sulphates but also with chlorides; the phenomenon was namely with chlorides also very distinct, though not so strong as in the case of sulphates.

This was always ascribed to the strong catalytic effect of Cl ions and the less one of the SO_4. Beck's measurements now show us that with magnesium not in inner equilibrium, SO_4 ions has also a powerful effect.

Although the highest potential shown in the last table (—1.816 V) is that of an active state of magnesium and the coexisting hydrogen must have been in a strong state of formation (strong overvoltage) yet this potential of Mg does not correspond with the inner equilibrium, for Mg containing small quantition of mercury shows a still higher negative voltage. This value was a maximum for 2 at $2\frac{1}{2}$ % Hg.

Now Beck found that the compound between Mg and Hg richest in the latter is Hg_3Hg and that the electrolytes in equilibrium with the various amalgams are practically free from mercury.

The influence therefore of the small quantity of mercury, under discussion on the Mg electrode can only he an activating one for the E—X fig. on the Mg side must be as follows (fig. 4). From this will be seen that if the influence of small quantition of mercury has not an activating one, then the potential of the amalgamated magnesium would have been less negative than that of the pure metal.

Thus activating by small quantities of mercury causes the true inner equilibrium to be approached more closely.

Magnesium which has been activated by mercury showed a potential of —1.856 Volts when placed in a solution containing 1 gr. mol. of $MgSO_4$ per liter.

Even this potential is below the equilibrium value owing to the disturbing effect, due to corrosion, but it is probable this is near the true equilibrium potential.

It is evident, that the potential of pure magnesium in true inner equilibrium must be more negative than that of the not disturbed amalgam, containing 2 at % Hg., because the E—X diagram

(fig. 4) shows us, that such potential is rendered less negative by increasing mercury content.

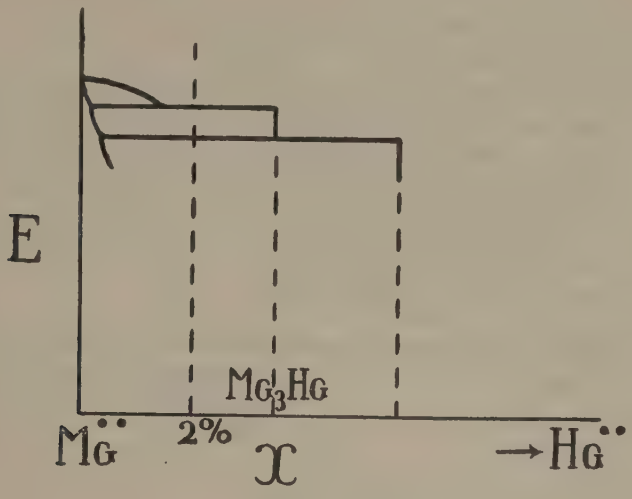

Fig. 4.

Finally we must consider a remarkable phenomenon to which brief reference has already been made.

If we add a little $HgCl_2$ in an aqueous solution of $MgSO_4$ or of $MgCl_2$ in which there is a magnesium electrode, there is an immodiate fine deposit of metallic mercury on the electrode whose potential becomes *less* negative.

As follows from the formula

$$\begin{array}{ccccc} Mg_s & \rightleftarrows & Mg^{\cdot\cdot}_s & + & 2\theta_s \\ \downarrow\uparrow & & \downarrow\uparrow & & \downarrow\uparrow \\ Mg_L & \rightleftarrows & Mg^{\cdot\cdot}_L & + & 2\theta_L \end{array} \quad \text{and} \quad 2\,\theta_L + Hg^{\cdot\cdot}_L \rightarrow Hg_L$$

The precipitations of mercury proves that mercury ions penetrate the surrounding liquid layer and that these on arrival combine with electrons, thereby disturbing the heterogenous equilibrium with the result that electrons and magnesium ions enter the solution.

It must also be observed that in consequence of the hydrolysis in the magnesium salt solution to which no acid has been added the magnesium electrode will contain dissolved $Mg(OH)_2$ and will consequenty behave inertly, so that by sending ions and electrons into solution, the potential of magnesium will be altered in the direction of that of the noble metals.

The experiment mentioned here is very important; it shows in the first place that the magnesium electrode notwithstanding its non

equilibrium state and the dissolved $Mg(OH)_2$ has still retained its metallic properties. Still its properties have altered, for the precipitated mercury is not able to activate it at once. An apparent explanation, namely that the precipitated mercury does not dissolve in the magnesium, is not correct.

For if we remove the magnesium electrode covered with fine mercury, prepared as above, wash it with distilled water and than dip it into pure $MgSO_4$ solution, the potential is at first less negative, but it becomes increasingly negative, so that after a few minutes it is stronger than that which attained before the negative electrode was coated with mercury.

This is shown in the following table

Solution	Mg-potential in relation to a 1-N-calomel electrode
0,1 gr. mol. $MgSO_4$ p. liter	— 1.902 V.
to 150 ccm. of the above mentioned solution is added 5 ccm. of a saturated solution of $HgCl_2$	— 1.740 V.

The magnesium electrode was then washed with distilled water and dipped into a pure solution of $MgSO_4$.

0.1 gr. mol. $MgSO_4$ p. Liter	— 1.898 V.
	— 1.956 V. after 5 minutes

The above data show that the magnesium electrode, though its surface is strongly disturbed by corrosion, has dissolved some mercury.

When we consider the great change brought about in a magnesium electrode by corrosion it is no wonder that its other properties, such as the power of dissolving mercury, are modified.

The explanation of the results in the above table now is clear. The activating influence exerted by the small quantity of dissolved mercury is not sufficient to decrease the retardation, exercised by the $Mg(OH)_2$ in such a way, that the electrode becomes insensible to the corrosive action of water and sublimate. When this solution has been substituted by one of pure $MgSO_4$ the influence of the sublimate disappears and that of the small quantity of mercury becomes manifest.

It might be supposed at first sight that in the experiment under consideration solid $Mg(OH)_2$ depositing on the magnesium electrode might diminish the contact between the magnesium and the mercury,

the fact is however that the contact between the magnesium and the electrolyte is so good that mercury is separated over the whole surface in a finely divided state, even whilst hydrogen is being given off.

At the same time it is clear, that if we wish to get a magnesium into as highly an active state as possible, it is desirable to make its surface as poor as possible in $Mg(OH)_2$ by first immersing it in an acid solution and then amalgamating it.

Magnesium, activated in this way, contains more dissolved mercury and even remains active in normal KOH, giving the high negative potential of — 1.97 volts in relation to the hydrogen electrode on account of the low Mg-ionic concentration.

In a solution containing 1 gr. mol. $MgSO_4$ per liter this electrode gave a potential of — 1.85 V. in relation to the hydrogen electrode.

Amalgamation experiments have also been studied in detail for Al and will be the subject of a next paper.

Amsterdam, Febr. 1923.

Laboratory for General and anorganic Chemistry of the University.

Botany. — "*A method of simultaneously studying the absorption of O_2 and the discharge of CO_2 in respiration.*" By D. S. FERNANDES. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of May 26, 1923).

Before entering into details, writer will briefly indicate, how the apparatus works and what precautions should be taken, illustrated by a simple diagram. (fig. 1).

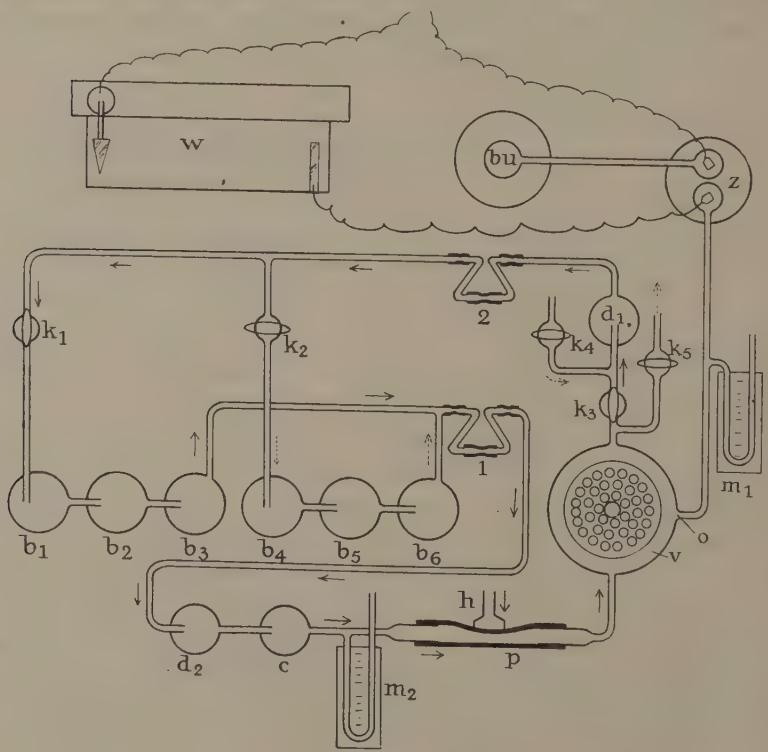

Fig. 1.

From p, a rubber sucking- and forcing pump, the air is pumped as the arrows indicate. The air enters the respiratory vessel v at the top, leaves it at the bottom and is dried in the wash-flask d_1, which contains concentrated sulfuric acid. From d_1 passing through

the glass cock k_1 (k_2 is then closed) it reaches the absorptiontubes b_1, b_2 and b_3, containing baryta-water. On its way back the air passes through the wash-flask d_2, containing sulfuric acid like d_1 and the control-baryta-tube c, after which it returns to p and recommences its circular course.

In a subsequent observation k_1 is closed and k_2 opened, causing the CO_2 absorption to take place in the tubes b_4, b_5 and b_6. The 6 absorption-tubes are fixed to a copper frame with clips. In order to enable us to take more than two observations, without bringing too many tubes in the glass vessel filled with water, which serves as a thermostat, we should have two of these frames at our disposal. If one has served its purpose, the connecting parts 1 and 2 are turned up and rise above the water, where they may be loosened. The whole frame with the 6 baryta-tubes is raised out of the vessel and the other (the tubes of which are meanwhile cleaned and filled each with 100 c.c. baryta-water) is put in. This exchange of frames is brought about in less than a minute, but before taking further observations with the newly-inserted baryta-tubes, we should wait (according to the temperature in the thermostat) 10—15 mins. that the tubes and their contents may adopt the temperature of the thermostat. The apparatus works ventilating during this time in the following way: Cock k_3 is closed, while k_4 and k_5 are opened. If next the pump is set working, the air, leaving the vessel, can only pass through k_5, while at k_4 air is sucked in, after having first been rid of CO_2 by means of wash-flasks containing strong KOH-solutions (not represented in the fig.). There is another advantage in the ventilating action of the apparatus. When in experiments of long duration the observations are stopped in the evening, the apparatus can continue to work ventilating the whole night. Consequently the objects are not subject to oscillations of temperature and the next morning the experiment may at once be continued by opening k_3 and closing k_4 and k_5. In experiments, lasting 10—12 hours, it saves a great deal of time, to put the plants into the apparatus the previous night, so that early in the morning the experiments can begin at once. After the ventilation during the night all CO_2 has been driven from the apparatus which may be demonstrated by blind experiments.

When the outer-air is shut from the apparatus, and the pump is set working, there is immediately produced an effective pressure on the vessel, while the manometer m_2, indicates a reduction of pressure. If next k_3 is opened, the air pressed in the vessel is blown off. On subsequent gradual closure of this cock, the pressure in the vessel

$= 1$. In the manometer m_1 the liquid is equally high in both limbs, whereas m_2 indicates a greater negative pressure than before. The broken equilibrium, generated by the action of the sucking-and forcing pump in the closed system is apparently shifted by the opening and closing of k_5 in such a way, that in the respiratory-vessel (accordingly on the plants) no effective pressure can arise. As soon as there disappears O_2 from the closed system through respiration, m_1 will indicate it at once. When however an equal quantity of O_2 is added at the same time, m_1 will remain at zero and the atmospheric pressure is preserved in the vessel. At O the oxygen, electrolytically produced in Z, enters the vessel. With the aid of the resistance w the O_2-development can be increased from a minimum to a definite maximum. The intensity of the electrolytic process may be thus regulated, that the O_2-production keeps pace with the O_2-consumption.

By increasing or reducing the resistance this equilibrium is soon found and the manometer m_1 indicates whether this condition is preserved. It may happen (for instance by rise or fall of the respiration-intensity), that for a moment there is a somewhat greater or smaller supply of O_2 to the apparatus. In this case the height of the manometer m_1, indicating as slight a difference as 0.1 cc., may at once be restored by means of the resistance, so that irregularities in the O_2 supply, amounting to more than 0,1 cc. need not occur.

The hydrogen simultaneously produced by the electrolysis in Z is collected in the burette *bu*. After necessary corrections (in height of barometer, temperature, water-vapour tension and pressure of the water-column in the burette) the quantity of hydrogen received, divided by 2, denotes the volume O_2, brought into the apparatus during the observation.

The manometer m_1 renders some other services. When a solution of kalium-jodide (with some soluble amylum) is used, m_1 is a sensitive test for the existence of spores of ozon. In the presence of this gas for instance the germ-plants of Pisum sativum do not develop normally, so that it is desirable to prevent ozon from entering the respiratory-apparatus.

Finally we have in the manometer m_1 a suitable test whether the desired temperature has been completely adopted by the whole apparatus as well as by the objects. If the observations are started before the whole has attained the desired temperature, the fluid will at once rise in the open limb of m_1, which signifies, that extension still takes place, while in consequence of the respiration (O_2 absorption) an immediate decrease of volume should appear.

For determining the period of preheating therefore m_1 is of practical interest.

The watervapour carried along from the vessel is combined in d_1 so that dry air enters the baryta-tubes. The watervapour taken from the lye is absorbed in d_2. By measuring the increase of volume in d_2 it may be found, how much water disappears from the lye and the titration standard may be corrected accordingly. This evaporation from the baryta-tubes is very slight and amounted to circa 2 cc. in experiments lasting 3 days, so that the correction may be left out without scruple.

The manometer m_2 is filled with mercury and serves to indicate the pressure, to be surmounted by the sucking and forcing pump, needed to drive the air through the various liquids. A drop of paraffine-oil on the mercury in the closed limb, prevents the originating of damaging mercury-vapours.

On the rubber-pump p taps a flat hammer h, moved vertically by an electro-motor (not represented in the figure). This hammer may be mounted higher or lower in order to regulate the capacity of the pump and consequently the size of the bubbles. The speed of the motor may be increased or decreased by means of a resistance, with which the regulation of the number of bubbles is possible. Size and number of bubbles are of course material to a good CO_2-absorption.

For an equable distribution of the air, entering the vessel, the ebonite plates on which the plants lie, are brought into a slow rotary movement by an axis. Accumulation of CO_2 in the vessel (see further on) is excluded in this way.

The suction of the air into and from the vessel, causes the liquid in m_1 to move up and down, which is not to be prevented. At an effective regulation of the pump this movement may be kept so slight, that it is no impediment. Indeed the motor may be stopped at any moment, to convince oneself whether the manometer is really at zero.

The whole apparatus is fixed to the inside of a copper frame and fits exactly in a glass vessel (contents about 45 L.), serving as a water-thermostat. Electrical heating enables us to keep the temperature of the water constant to 0.03° C. The oscillations of temperature in the apparatus itself are slighter than those in the thermostat, so that corrections relating to this, may be omitted.

If the apparatus is immersed in the water of the thermostat, it may be easily tested with respect to air-tightness. For this purpose air is pumped into the apparatus through k_4 and one watches whether

any bubbles rise from the water. When the connections are made with vacuum rubber-tube and glass to glass, leakages do not occur.

II.

Descriptions of the parts.

a. Sucking- and forcing-pump (fig. 2).

An air-tight pump, working for a long period without failing and having a sufficient capacity, is easily constructed.

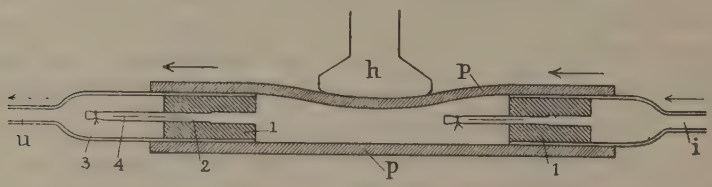

Fig. 2.

The glass tubes *i* and *u* are connected by a piece of strong rubber-tube *p* (about 15 cms. long and $2^1/_2$ cms. wide). Each of the tubes *i* and *u* is provided with a valve, consisting of a piece of vacuum-tube (1 cm. long) 1, to which the end of a piece of valve-tube 2 (about 3 cms. long) is glued on with solution. The other end of the valve-tube is tightly tied with a string at 3; in the valve-tube a straight lengthwise cut 4 is made, the two edges of which meet, when the pump does not work. To prevent these edges from sticking together afterwards, they have been rubbed in with talcum powder. The glass tubes *i* and *u* fit in the rubber-tube *p*, while the vacuumpieces 1 must also fit perfectly. How the pump works, when the hammer *h* taps on it, is clear from the fig. 2.

b. The respiratory-vessel (fig. 3).

As in KUYPER's research[1]) here too is made use of a copper cylinder 1. The experimental objects are on the ebonite plates *t*, fixed to an axis a_2. In each of the plates *t* 25 round holes are made in such a way, that germinating seeds of Pisum sativum cannot fall through. On the plates t_1 moist cotton-wool is put, on which the roots rest, in consequence of which there cannot occur a deficiency of water. The axis a_2 is enlarged at the top, provided

[1]) KUYPER J: Recueil des Travaux Botaniques Néerlandais. Vol. VII. 1910, pag. 1.

with 4 teeth ta, just fitting into the four teeth ta_1 belonging to a simular enlargement at the base of the axis a_1. This steel axis a_1 passes through a copper case k (soldered to the cover), in which it

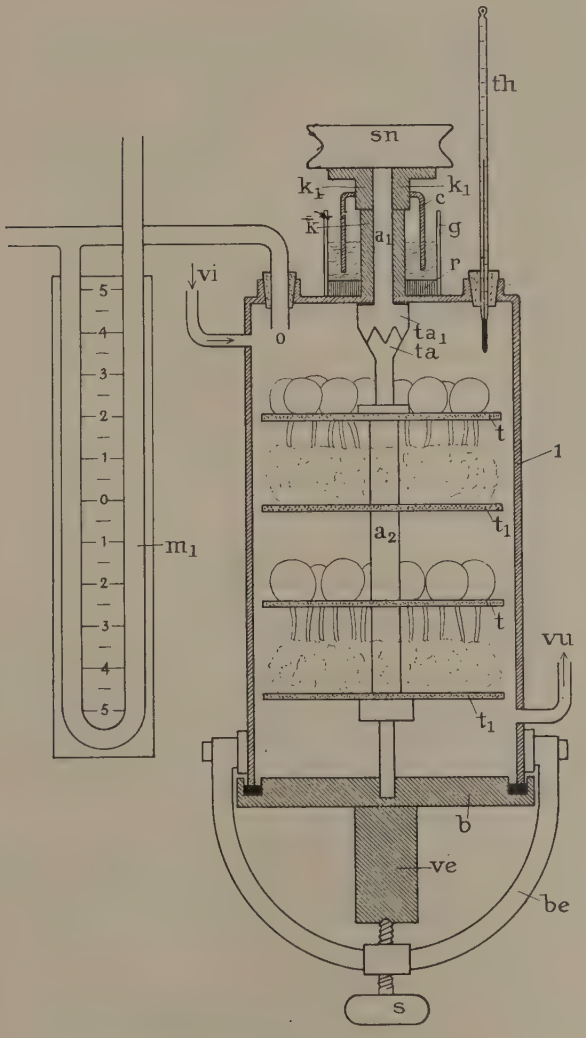

Fig. 3.

fits exactly, but may be easily rotated. Round k there is a glass cylinder g, closed at the bottom by the india-rubber-ring r. The axis a_1 is at the top tightly clasped in a copper tube k_1, at the bottom of which the hollow metal cylinder c is fastened, and at the top the grooved wheel sn. By the oil in g the axis is closed

off air-tight and leakage is impossible, because there never arise great differences of pressure in the vessel. In the middle of the loose part *b* there is a cavity, in which a_2 can rotate freely. When *sn* is slowly rotated by a motor, a_1 will transmit this movement by means of the teeth ta_1 and *ta* to a_2, which causes the circulating air to be equably distributed over the whole vessel, in consequence of which the germplants are constantly surrounded by fresh air. The necessity of ventilation in a cylindrical respiratory vessel (diameter 15 cms., height 20 cms.) was immediately apparent from one of the many test experiments. At a constant temperature of 20° C. the O_2-absorption caused in 50 mins. a height of 4 cms. on the manometer m_1. Next a quicker circulation of 10 mins. duration followed, causing an equal rise of the manometer as before in 50 mins. No other explanation of this could be found, but the occurrence of a CO_2-accumulation in the vessel. This was supposed to be due to the fact, that the air entering at *vi* passed by the easiest route through the vessel to the exit *vu*, taking with it only part of the CO_2. When in consequence of a more rapid circulation part of the accumulated CO_2 disappeared, this explained a sudden greater rise of the manometer. As soon as the rotary movement of the respiring objects, prevented all CO_2-accumulation in the vessel, there was indeed no abnormal rise of the manometer to be noticed. It needs no argument, that not only with a view to oxygen-supply and measurement, but also for other reasons, the CO_2 due to respiration, should be directly removed. With a CO_2-accumulation in the vessel, a volumetric determination of the vanished quantity of O_2 is no more possible. Besides in this case part of the plants gets into an atmosphere full of CO_2 and deficiency of O_2 will soon cause intramolecular respiration.

It seems to me, that in the respiratory apparatus after the model given by PFEFFER and DETMER and used e.g. by KUYPER, little or no attention has been paid to the error which may be committed, when in a respiratory vessel as described in this paper, no perfect ventilation is provided for.

The loose bottom *b* is provided with a marginal groove, containing a rubber-ring. The handle *be* bears in its middle a screw *s*, which, when turned up, presses on *ve* and by doing so presses the lower edge of the vessel tightly in the groove with rubber-ring.

In the cover of the vessel is, besides the aperture *o* to admit oxygen, also a pierced rubber-cork through which a thermometer *th* passes.

c. Fig. 4 gives a representation of the *drying-tubes* and the

control-tube. Cock 1 serves for filling, cock 2 for emptying and cleaning.

d. The *absorption-tubes* are fastened to a copper frame (fig. 5). As with a view to preversing a constant temperature the size of the thermostat cannot be chosen at will, straight absorption-tubes (length 25 cms., width 3 cms.) are more suitable than PETTENKOFER or WINKLER-tubes. When baryta-water is chosen for combining with CO_2 (21 grammes of bariumhydroxyde + 3 grammes of barium-chloride in 1 L. of water), the absorption is only complete, when the air passes through 3 of those tubes (each containing 100 cc. lye). Each frame of 6 tubes therefore can only serve for two observations. The tubes end at the base in thin open pieces, which may be plugged by rubber stoppers. At the top they are closed by rubber-corks 3 cms. thick. In each cork there are three holes, two of which serve for the inlet- and exhaust-tubes, while the third, which serves for filling can be plugged by a little massive glass bar. The tubes are connected with vacuum-rubber

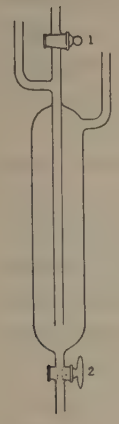

Fig. 4.

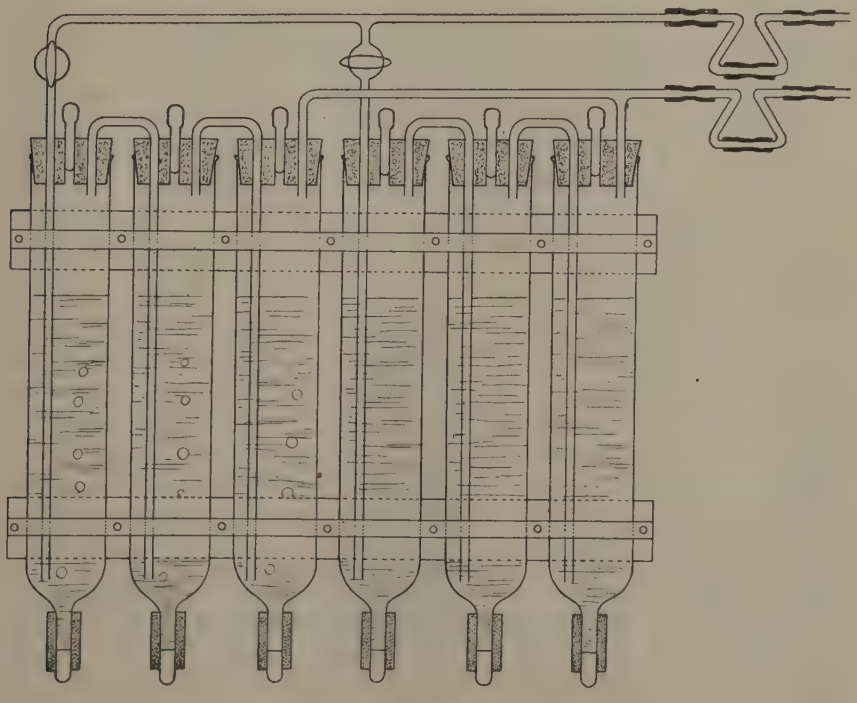
Fig. 5.

tube, just as all other connections in the apparatus are made. There was no sign of any CO_2 diffusion inward from the water of the thermostat through the rubber-connections and corks, nor of an O_2-absorption through the rubber. Blind experiments, lasting 24 hours gave no measurable change of titration standard of the lye at temperatures between 20° and 30° C., while the manometer m_1 remained at zero throughout that time.

e. The oxygen-supply and measurement.

In order to prevent ozon-formation, a 10 % natronsolution is to be preferred to diluted sulfuric acid for the electrolysis.

In fig. 6 *C* is a glass cylinder with natron-lye in which the platina-electrodes p_1 and p_2 are placed. By means of thin platina-wire these electrodes are fastened by melting in the glass-tubes 1 and 2 respectively. The tubes 1 and 2 pass through caoutchouc-

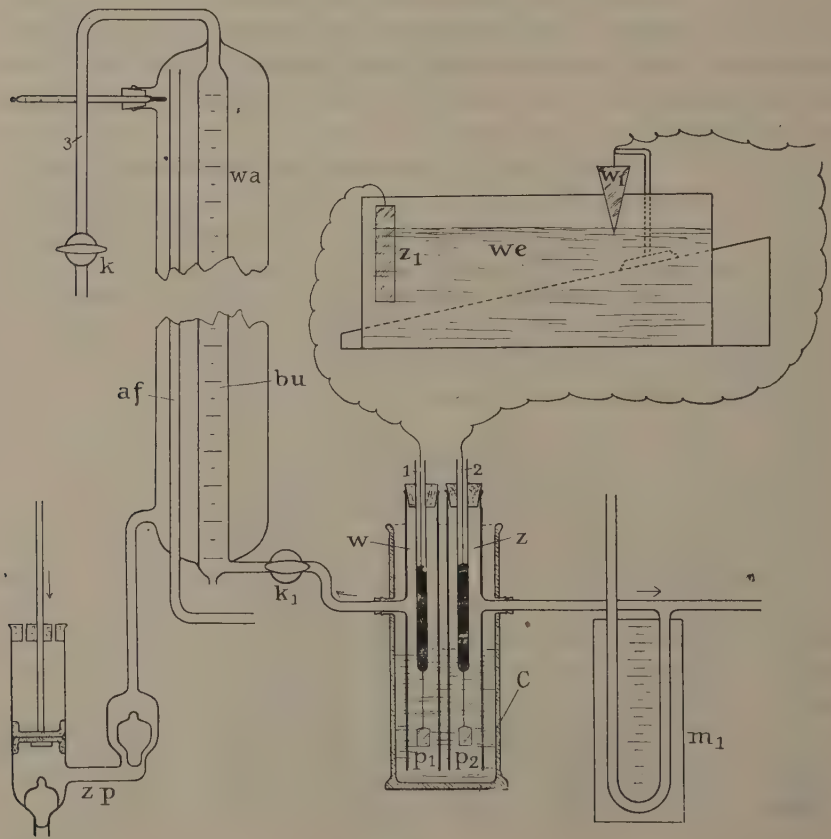

Fig. 6.

corks, fitting exactly in the wider tubes *w* and *z* (open at the bottom) and are filled with some mercury. By means of a resistance *we* the intensity of the current can thus be regulated, that the amount of the electrolysis can reach the desired extent. Thus it is possible to keep the oxygen-development, occurring in the tube *z* at the electrode p_2, in balance with the O_2-consumption of the respiration. As a resistance (*we*) a glass basin with water, in which the electrodes w_1 and z_1, is quite satisfactory for this purpose. By moving w_1, which is fastened to a stand, along a sloping board, not only the distance $w_1—z_1$ is made smaller or larger, but this electrode also goes more or less deep in the water.

The O_2 formed in *z* is in open connection with the manometer m_1 and the respiratory-vessel. The tube *z* really is likewise a manometer, in which the lye will be equally high as in *c*, when the quantity of O_2 developed is equal to the quantity disappearing in the apparatus; m_1 however, as already mentioned, is necessary to control the ozon-formation.

For receiving the hydrogen, formed at the electrode p_1 in the tube *w*, the burette *bu* serves, which gives accurate readings to 0.1 cc. This burette ends at the top in a bent glass tube 3, provided with a glass cock *k*. At the bottom the burette has a narrow aperture, while not far from this a lateral tube has been fitted on, forming a connection with the tube *w*. When the burette is placed in such a way, that the bottom aperture lies just below the water-level in the thermostat, it is impossible, that while water is flowing out, air is ascending in the burette at the same time. Filling the burette with water from the thermostat is done by closing k_1, opening *k* and sucking at the tube 3. When after filling *k* is closed and k_1 open, the only reason why water should flow from the burette, is the formation of hydrogen in *w*, which rises in the full burette as bubbles. The formation of the first hydrogen-bubbles in the burette requires a little effective pressure, which is shown by the fall of the fluid in the tube *w*. This effective pressure, which remains constant during the emptying of the burette, should exist before the observations begin, lest the first reading should give a too small figure. This error is prevented, when some minutes before the experiment commences — when the apparatus still works ventilating — the electrolysis is made to take place, till the first bubbles rise in the burette. In case that, during one and the same observation, the burette is filled several times, the sucking up of the water should occur very slowly and equally, lest the hydrogen, which is in the connective-tube between k_1 and the burette, should be sucked in

with it. If the water is sucked cautiously into the burette, the effective pressure once made is preserved in *w*.

Another error arises, when the burette is exposed to oscillations of temperature in the laboratory. In that case not only in *w*, but also in *z* and m_1 falls and rises occur, which are not due to absorption of oxygen. This may be prevented by keeping the burette likewise at a constant temperature, which may be attained as follows.

By means of a metal sucking- and forcing-pump *zp* (likewise fastened to the copper frame, to which the whole apparatus is fastened) water from the thermostat is pumped up with great rapidity into a wide glass cylinder *wa*, which contains the burette. The water enters *wa* at the bottom and is led back to the thermostat at the top through the tube *af*. Even at high temperature (50°, 55° C.), the temperature in the burette is kept equal to that of the water in the thermostat in this way.

f. The regulation of the temperature principally corresponds to the one described by RUTGERS[1]) and COHEN STUART[2]) and is an imitation of apparatus, used in the VAN 'T HOFF-laboratory at Utrecht.

The heating-apparatus *v* (fig. 7) consists of a copper case, surmounted by a metal tube, rising above water. In *v* is paraffine-oil, electrically heated by a nickel-chrome-wire, wrapped round a piece of mica.

Thermoregulator *t*, stirring-apparatus *r* and *v*, are close together in an open glass cylinder *c*, resting on legs in the centre of the thermostat *g*. To prevent all influence of vibration in the height of the mercury, the thermoregulator is hung from the ceiling on a steel spiral-spring, according to the method MOLL.

The method described above gives no new principle, with respect to the CO_2-determination. We have chosen the simple and always trustworthy baryta-method, which need not be further described here. On account of the insertion into a closed system, the various parts were subjected to some alterations in shape, which however have nothing to do with the principle of the baryta-method.

The problem of oxygen-supply, ever yielding many difficulties, could be satisfactorily solved. Compared with the methods[3]) already existing, the following advantages and simplifications are achieved:

[1]) RUTGERS, A. A. L., Recueil des Travaux Botaniques Néerlandais. Vol. IX, 1912, pag. 1.

[2]) COHEN STUART, Recueil des Travaux Botaniques Néerlandais. Vol. XIX, Livraison 2. 1922.

[3]) Cf. KROGH: "The respiration exchange of animals and man. LONGMANS, GREEN and Co., London 1916".

a. the decrease of pressure and oxygen-content in the apparatus is reduced to a minimum.

b. the place of the consumed O_2 is at once taken by pure O_2, without first passing a stop-valve, and may directly be controled.

c. an oxygen-bomb or other reservoir may be omitted.

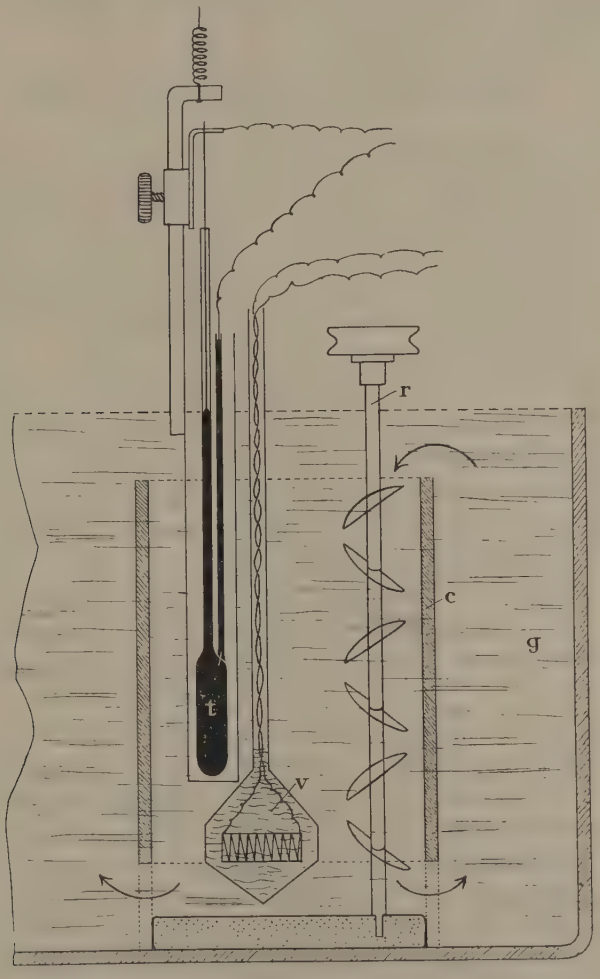

Fig. 7.

The apparatus has been constructed by Mr. P. A. DE BOUTER, amanuensis at the Botanical Laboratory at Utrecht. I am greatly indebted to him, not only for the way, in which he performed his task, but also for introducing some clever improvements.

Utrecht, May 1923. *Botanical Laboratory.*

Physiology. — "*A new form of correlation between organs.*" By Prof. H. J. HAMBURGER.

(Communicated at the meeting of May 26, 1923).

Thus far we were acquainted with two forms of cooperation between organs. As to the eldest known form, here the central nervous system plays an important rôle. If any one pricks my finger unexpectedly with a needle, I immediately withdraw my arm; a cooperation has taken place between the skin of the finger and the muscles of the arm, and well by means of the spinal chord. Here we have to deal with a reflex.

Some years ago we got acquainted with a second form of correlation between organs; this one is not effected by means of nerves, but here the bloodcurrent is the mediator of the cooperation. For instance, the glandula thyroidea produces substances, which are carried through the body by the bloodcurrent and influence the metabolism and growth of distant organs.

That nerves here don't play an essential rôle appears from the fact, that the glandula thyroidea still exerts its influence, even when it is detached from its nerves and transplanted to another part of the body.

Now, in the last years experiments, performed in our laboratory, have clearly demonstrated *a third new form*[1]) *of correlation between organs*. The starting point of these researches, carried out by Dr. R. BRINKMAN, Miss E. VAN DAM and Dr. L. JENDRASSIK, was the following experiment of O. LOEWI in Graz. The vagus nerve of an isolated frog's heart, which is filled with a salt solution, is for some time stimulated so that the heart stops its beat. Then the content of the heart is removed and transferred into another frog's heart, which was isolated in the same way. Then the well-known pharma-

[1]) See my lecture at the opening of the Biological Buildings of Mc. Gill's University in Montreal (Canada) in September 1922. See also: H. J. HAMBURGER. The increasing significance of permeability problems for the biological and medical sciences; the Charles E. Dohme Memorial Lectures. First Course, 10, 11, 12 October 1922, delivered in Baltimore; printed in: Bulletin of the Johns Hopkins Hospital, June 1923.

cologist saw, that the second heart often showed slower contractions. Experiments with the sympathetic nerve gave analogous results.

Now the purpose of our experiments was in the first place to control the results of LOEWI's researches under more physiological conditions.

In the vena cava of a frog A a glass tube is inserted and in this way a suitable saltsolution is conducted through the heart. A similar small tube is introduced into the aorta. Then we see, that the saltsolution will leave the heart in a rhythmical manner. If then the fluid, leaving the heart, is led to the vena cava of another frog B, the fluid will run through the heart B, and after leaving it by the aorta of this second frog, it may be taken up again by the vena cava of the first frog A. Thus we obtain a circulation of saltsolution through both frog's hearts. This method of socalled "crossing circulation" was first introduced by Prof. J. C. HEMMETER.

Now, if the sympathetic of the first frog A be stimulated electrically, causing acceleration of the heart beat of this frog, it can be observed that already after a few seconds, the heart rate of the second frog B is also quickened, *although the sympathetic of this animal has not been stimulated.* How to account for the acceleration of the second heart? Evidently in no other way than by assuming that in the first heart A, in virtue of permeability of course, substances were liberated which had a similar effect upon the second heart as if this had been directly stimulated. I shall presently come back to the probable nature of these substances.

How it is possible that substances, liberated by a physiological action of an organ, here the heart of the frog A, may also stimulate the same organ of the second animal B, I shall not discuss here. It is sufficient to say, that there is an analogy between this case and the secretion of saliva. If we allow a salt solution to percolate through the salivary gland, as J. DEMOOR has demonstrated some years ago, no saliva is secreted. However it does occur if a small quantity of saliva is added to the saltsolution. The product formed during the activity of the salivary gland is, it seems, a stimulus again to further secretion of saliva. The substances, formed in the stomach during conversion of protein, excite gastric secretion. It is therefore not strange that the substances, liberated in the first heart during stimulation of the sympathetic, should have a stimulating action on the second heart.

Dr. BRINKMAN and Miss VAN DAM made yet another experiment that in a still more convincing and striking manner demonstrates, that the transmission of stimuli can take place by means of fluids,

in other words that there exists a humoral transmission[1]), I say "in a still more convincing manner", for by the just mentioned experiment the remark could be made, that with the movement of the second heart hydrodynamic influences might have played a rôle.

For this reason for the second organ not the heart of the frog B was taken, but the *stomach* of this animal.

It is well known that stimulation of the sympathetic nerve is followed not only by an acceleration of the heart beat, but also it slows, even inhibits the spontaneous movements of the stomach. Now the question arose: if the fluid of the stimulated heart of frog A is transferred into the arteria gastrica of the frog B, will it then cause the spontaneous movements of the stomach of this last frog to grow slower, even to stop? This proved to be the case, as the experiments of Dr. BRINKMAN and Miss VAN DAM showed us. *In other words, on sympathetic stimulaiton of the first heart substances were liberated which influenced the movements of the stomach in an inhibitive way.*

Analogical phenomena as occur in stimulating the sympathetic nerve could be observed by stimulation of the vagus nerve.

As it is well known, stimulation of this nerve affects the rate of the heart beat and also influences the strength of the contractions of the stomach, but in an antagonistic sense. Stimulation of the vagus slows the heart, but causes the contractions of the stomach to become more powerful, contrary to what happens when the sympathetic nerve is stimulated. Now the experiment was repeated by crossing the circulation of the heart of the first frog with that of the stomach of the second frog; in other words, the salt solution coming from the heart of the first frog, is conducted to the stomach-circulation of the second frog. On stimulating the vagus of the first frog, the heart slows its beat and when the solution has passed through this heart and reached the stomach of the second frog, this organ shows typical vagal contractions, though the vagus of frog B has not been stimulated electrically. From this we may infer that stimulation of the vagus of the first frog sets free in its heart vagus-substances, which may cause the stomach of the second frog to contract, as if its own vagus nerve had been directly stimulated.

We are therefore in presence of two kinds of substances liberated by the vagus and sympathetic nerve respectively, which may be called vagus- and sympathetic substances.

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[1]) R. BRINKMAN und Frl. E. v. DAM, Pflüger's Archiv. Bd. 196, S. 166, 1922.

That really such substances exist, could be directly proved by the fact that the salt solution, leaving the heart after stimulation of the vagus, contains substances, which lower the surface-tension of the original salt solution, socalled capillary-active substances. On the other hand we find that the surface-tension of the salt solution, coming from the heart after the sympathetic nerve has been stimulated, is slightly increased [1]). Further it appeared that the vagus- and sympathicus-substances were able to neutralize each other in capillary-active sense, i. o. w. they were able to neutralize each other's influence on the surface-tension.

I shall not enter here into further particulars. It is an established fact now, that as an effect of stimulation of the vagus nerve, a liberation of vagus-substances takes place, and that on stimulating the sympathetic nerve, sympathetic-substances are set free. However the nature of these substances has not yet been determined; perhaps, at least with the vagus-stimulation, we have to do with cholin-compounds, which cooperate with the potassium.

As for the method to determine the surface-tension of very small quantities of fluids, we refer to two articles, which appeared last year [2]). There it is shown that a very simple apparatus will do for this purpose. By means of a torsion balance, well-known to the clinicians, the force is determined which is necessary to pull off a small platina-ring from the surface of the fluid which is to be examined.

The experiments discussed here, give rise to many questions. So the clinician will think of the bearing of these results on the nature of vagotonia and sympathicotonia and will ask himself under which conditions an excess of vagus- and sympathicus-substances will exist in the circulation and influence different organs; and also he will put himself the question how it will be possible to make this surplus harmless for the body.

The physiologist will ask himself whether the latent period and the after-effect in vagus-stimulation can be explained by the time, which is necessary for the liberating and the disappearing of the vagus-substances; further he wants to know whether the vagus-substances are specific for one and the same animal. And what will be of interest both for the physiologist and the clinician is the question: can we observe the same phenomena, seen in the frog,

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[1]) See the article of Dr. BRINKMAN and Miss VAN DAM, in the Journal of Physiol., still to appear.

[2]) R. BRINKMAN und Frl. E. VAN DAM. Münch. Med. Wochenschr. 1921. S. 1550.
R. BRINKMAN, Arch. Néerl. d. Physiol. VII 1922, p. 258.
R. BRINKMAN und Frl. E. VAN DAM VIII, 1923, p. 29.

also *in warmblooded animals?* With this question Dr. L. JENDRASSIK has occupied himself very recently. The results obtained untill yet, can be summarized in a few words. If the surviving heart of a rabbit is perfused with a suitable salt solution, and we stimulate the vagus nerve, then the liquid, leaving the stimulated heart is able to accelerate in a high degree the contractions of an isolated piece of gut, taken from the same animal.

I cannot enter into these researches on this place. Dr. JENDRASSIK will describe them in a short time in the Biochemische Zeitschrift. Here we will only point out that the experiments proved, that on stimulation of the vagus nerve not only in the heart of coldblooded animals but also in those of warmblooded animals substances are produced, which are able to influence other organs in the very same way, as if the vagus of those organs were stimulated by an electrical current. Here the gut proved to be the most suitable object for the researches.

Further I might draw the attention of the readers to three remarkable facts. In the first place it appeared that an extract of the atrium of a rabbit's heart in saltsolution was also able to accelerate the contractions of the isolated piece of gut. This experiment was made in considering that it would be very probable, that the atrium still contained vagus-substances, which were formed there during the life of the animal. Secondly it appeared that if atropine, which, as is well known, inhibits the influence of vagus-stimulation, was added to the active extract, this was turned into an unactive one, i.o.w. then it had no more influence on the movements of the gut. In the third place it was found, that the extract of the ventricle-muscle of the heart has a sympathetic effect on the movements of the gut instead of a vagus-influence.

The experiments on warmblooded animals described above, were all performed in a room of body temperature.

SUMMARY.

Thus far we have been acquainted with only two forms of correlation between organs, one, the eldest, established through interference of the central nervous system in cases where a quick response is needed (reflexes). The second form comes into play where slow processes are concerned; it may be exemplified by the influence of the glandula thyroidea on metabolism and growth. For the formation of hormons the influence of the nervous system is not needed, neither for the transport by the bloodcurrent. In *the third new form*

of correlation the action is neither quick nor slow; it is to be seen at work where functions, holding the medium between these two, are concerned. The essential thing here is, that *by nervous stimulation* substances are set free, which are conducted to other parts of the body.

There is much evidence to lead to the belief that the three forms may finally by reduced to one, but I cannot enter into this here. I have spoken about this possibility already in one of my HERTER-LECTURES, delivered in New-York in October 1922.

It may be of importance to lay stress on the fact that the formation of vagus- and sympathicus-substances is not only postulated, but *that it is proved directly in a physico-chemical way.*

There is no doubt that an analogous correlation between organs as described here for heart and stomach and for heart and gut will be established also between other organs[1]). We face here a wide field of new researches; we are only in the beginning.

May 1923. *The Physiological Laboratory of the University of Groningen.*

[1]) So it appeared very recently in our laboratory, that when stimulating the nervus vagus and the nervus sympathicus of the heart, substances are set free, which influence the *lumen of the small arteries* of another animal. (Note after the correction).

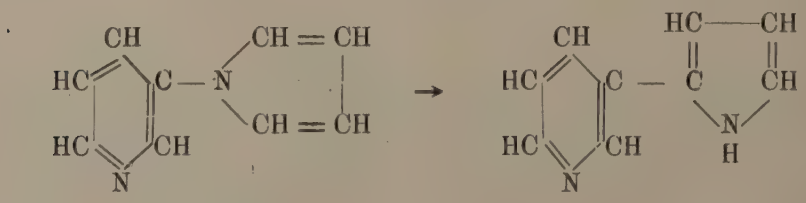
Chemistry. — "*The Synthesis of some Pyridylpyrroles.*" By Dr. J. P. WIBAUT and Miss ELISABETH DINGEMANSE. (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated at the meeting of March 24, 1923.)

In the course of the researches on the structure of the natural alkaloids, several of these vegetable bases have been prepared by synthesis. In other groups of vegetable substances, investigators have not only succeeded in building up the substances occurring in nature, but also closely allied bodies were obtained synthetically. In the group of the sugars, e.g., a number of monoses have been obtained which do not occur in the vegetable kingdom, but which are isomeric with or closely related to the sugars found in nature. Our knowledge of the chemical and biochemical properties of the monoses has been greatly improved by these synthetic researches. It seems not devoid of interest to try and build up an isomer of a natural alkaloid, in order to examine afterwards in what respect the isomeric substance is distinguished from the natural alkaloid, especially with regard of physiological and biochemical properties.

Keeping this end in view we will try to build up an isomer of nicotine.

In his synthesis of nicotine PICTET started from β-amino-pyridine; this substance was heated with mucic acid, through which N (β-pyridyl)-pyrrole (I) was obtained. At high temperature N (β-pyridyl) pyrrole undergoes an isomerisation, in which C (β-pyridyl)-pyrrole (II) is formed:



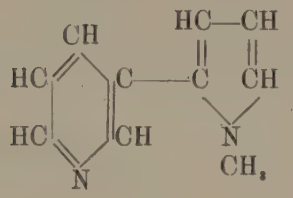
I. II.

PICTET and CRÉPIEUX [1]) give the above structure to this C (β-pyridyl)

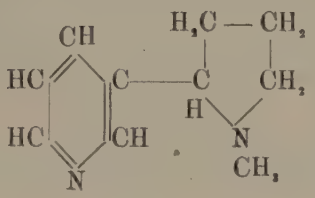
[1]) Ber. d. deutsch. chem. Ges. **28**, 1904 (1895).

pyrrole, in which it is, therefore, assumed that the pyridine nucleus is united at the α C atom of the pyrrole nucleus.

In how far this assumption is justified, will be discussed afterwards. The preparation of these substances did not offer any special difficulty; on the other hand, the conversion of C(pyridyl) pyrrole (II) into the methyl derivative, nicotyrine (III), was difficult to realize:



III.



IV.

When it is tried to methylate the pyrrol derivative at the nitrogen atom by treating the potassium-compound with methyl-iodide, there is also a molecule of methyl iodide combined with the nitrogen atom of the pyridine nucleus, so that the iodine methylate of nicotyrine is formed, from which afterwards methyl iodide must be split off.

PICTET and ROTSCHY [1]) have obtained but very little of the nicotyrine by this method. For the continuation of his experiments PICTET has, therefore, made use of a nicotyrine preparation which was prepared by oxidation from nicotine (IV) by BLAU's method.

A similar procedure is of course impossible in our case. In the end PICTET and ROTSCHY have succeeded in reducing nicotyrine to nicotine by an indirect way through making use of iodine and bromine substitution products.

Hence if this synthesis is repeated, starting from α-amino-pyridine, an isomer of the nicotine can be built up, in which the pyridine nucleus is substituted at the α-place.

As α-amino-pyridine is at present an easily accessible substance, it seemed not impossible to obtain sufficient quantities of all the intermediate products, so that it may also be expected that it will be possible to prepare so much of the final product that its properties can be properly studied.

§ 2. *The preparation of N-(α-pyridyl)-pyrrole.*

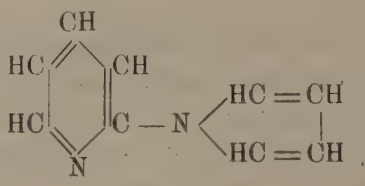
For the preparation of N-(α-pyridyl)-pyrrole we have heated 25 gr. of α-amino-pyridine with 28 gr. of mucic acid. First the salt of

[1]) Ber. d. deutsch. chem. Ges. **37**, 1225 (1904).

mucic acid with 2 mol. α-amino-pyridine is formed. At a temperature of about 140° this salt begins to decompose: with separation of water and carbon dioxide the pyrrole derivative is formed while 1 mol. amino pyridine is split off. Hence a distillate is obtained which contains besides water, the required pyrrole derivative and amino pyridine. We have subjected the reaction product to fractionated distillation at 15 m.m. pressure. The first fraction of 104—130° is chiefly α-amino pyridine. At 140—145° distills a liquid, of a slight yellow colour, which solidifies to a white crystalline mass on being cooled in ice. The melting-point of these crystals is 17° C.

This substance is N-α(pyridyl)-pyrrole, to which the following structure formula (V) applies.

V



The freshly distilled N-(α-pyridyl)-pyrrole is a colourless liquid, which, however, assumes a dark colour after some time. The boiling-point at 760 mm. lies at 260—261°.

This substance is sparingly soluble in cold water, volatile with water vapour, and readily soluble in all organic solvents. A pine-chip moistened with hydrochloric acid is coloured red-violet by the vapour of N-(α-pyridyl)-pyrrole; with a hydrochloric acid solution of dimethylaminobenzaldehyde there arises a red-violet colour, which later on changes into a dirty green. These colour reactions are considered as characteristic of pyrrol derivatives. By potassium permanganate this compound is rapidly oxidized already at the ordinary temperature.

The values of 19.58 % N and 19.34 % N were found for the nitrogen percentage of this preparation, the calculated percentage for $C_9H_8N_2$ being 19.44 %. We have prepared a picrate of this substance which melts at 143°. We obtained the iodine methylate of the N (α-pyridyl)-pyrrole by heating it in a sealed tube at 100° with the calculated quantity of methyl iodide. The reaction product was recrystallised from alcohol: yellowish white prisms, melting-point 141°—142°.

The isomeric N (β-pyridyl)-pyrrole prepared by Pictet and Crépieux has been described by these investigators as a liquid with

a boiling-point of 250.5—251° at 730 mm., which does not solidify at —10°.

The yield of N(α-pyridyl) pyrrole was in our experiments from 7 to 8 gr. out of 25 gr. of α-aminopyridine.

We found, however, that there is formed another substance besides this pyrrole derivative in the reaction between mucic acid and amino pyridine. During the distillation of the reaction product a liquid went over at 170°—190° and 15 mm., which crystallized at room temperature. After recrystallisation from alcohol this substance had a melting-point of 95°, and appeared to be α-α'-dipyridyl amine. The formation of this compound during the heating of the mucic acid salt of amino pyridine seems to be analogous to the formation of diphenylamine from aniline and hydrochloric aniline.

We have actually obtained α-α-dipyridyl amine by heating equivalent quantities of α-amino pyridine and the hydrochloric acid salt of this base in a sealed tube for two hours at 300°. We hope to return to this reaction on another occasion.

§ 3. *The conversion of N(α-pyridyl)-pyrrole into two isomeric C(α-pyridyl)-pyrroles.*

It was found long ago by Ciamician [1]) and his collaborators that the N-derivatives of pyrrole can be transformed into C-derivatives by the action of high temperatures.

Ciamician and Magnaghi [2]) heated N-acetyl pyrrole in a sealed tube at 250—280° and found that part of the starting material was changed into pyrryl methyl ketone:

That the acetyl rest actually occupies the α-position in the pyrrole nucleus, results from the observation that the bromation product of this pyrryl methyl ketone yields the imide of di-bromomaleic acid by oxidation with nitric acid [3]). Also some other pyrrole derivatives, in which an acylrest is combined with the nitrogen atom, were transformed into α-pyrrylketones on heating.

It was found later by Pictet and his collaborators that N-methyl pyrrole, N-phenyl-pyrrole, and similar substituted derivatives of

[1]) Cf. Ciamician. Ber. d. deutsch. chem. Ges. **37**, 4200 (1904).

[2]) Ibid. **18**, 1828 (1885).

[3]) Ciamician and Silber. ibid. **20**, 2594 (1887).

pyrrole can be transformed into C-derivatives by distillation through a red-hot tube.

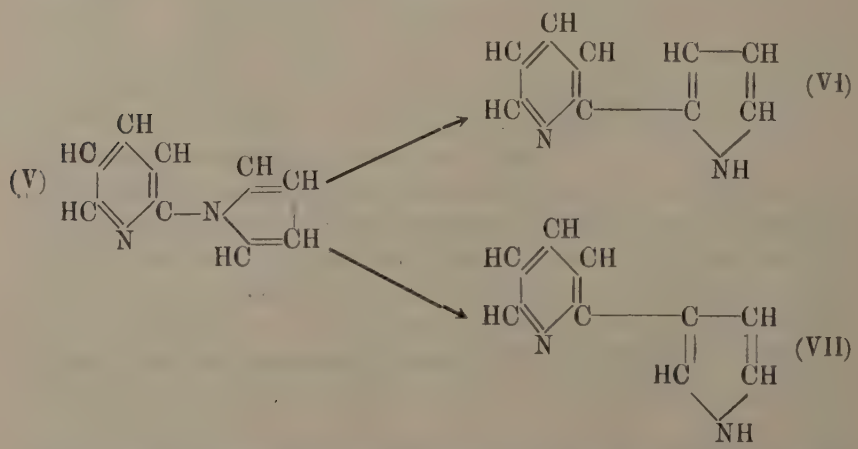
In all these intra-molecular arrangements only one C-derivative was found, whereas it would be theoretically possible that two isomeric pyrroles would be formed, since the hydrocarbon rest might be united at the α- or at the β-carbon atom of the pyrrole nucleus.

From N-methyl pyrrole the α-C-methyl pyrrole was obtained by PICTET. The structure of α-C-methyl pyrrole had already been determined by ZANETTI, by converting this substance into the dioxime of levulic aldehyde.

PICTET and CRÉPIEUX assume on grounds of analogy that in the C-phenyl pyrrole which they obtained from N-phenyl-pyrrole, the phenylgroup is united at the α-carbon atom of the pyrrole nucleus, and that the same thing holds for the C-pyridyl pyrrole (II), which they obtained from N-β(pyridyl)- pyrrole (I). A direct experimental evidence, for this view was not given.

As regards PICTET and CRÉPIEUX' β-pyridyl-α-pyrrole, the structure which these investigators assign to it, is undoubtedly supported by the fact that they have obtained nicotyrine (III) from this β-pyridyl pyrrole, as the structural formula (IV) of nicotine has been made very probable by PINNER's researches.

We found however that two isomeric C-pyridyl-pyroles are formed in the transformation of N(α-pyridyl) pyrrole, one of which melts at 93° and the other at 132—132.5°. This reaction must be represented by the following scheme:



To which of our isomers formula VI applies and to which formula VII should be assigned, has not yet been established. It

will not be very easy to decide this point. In former researches it has been tacitly understood that in the transformation of a N-derivative of pyrrole in a C-derivative, it is always the α-compound that is formed. In consequence of our observations the validity of these conclusion has become doubtful.

We shall now give a short description of our experiments on these reactions.

In the first place we have determined the most favourable temperature for the transformation of N(α-pyridyl) pyrrole into the C(α-pyridyl) pyrroles, as in PICTET's papers the reaction temperature is only vaguely indicated as "heated to redness" or "faintly red-hot". The best procedure appeared to be as follows:

25 gr. of N(α-pyridyl)pyrrole are distilled through a glass tube filled with pieces of pumice, which is heated at 670°—690° C. in an electrical oven. Part of the substance is decomposed, which shows itself in the formation of dense white vapours. The distillate consists of a black liquid, which soon solidifies at room temperature. This reaction product was distilled with steam, in which a white crystalline substance passed over, which was filtered off. This substance appeared to be very sparingly soluble in cold water. The crude product melted at 84°; after recrystallisation from a mixture of benzene and ligroine the melting-point is 90°. The yield of this substance was about 12 gr. The aqueous distillate contained only very little unchanged N(α-pyridyl) pyrrole. A second substance remained behind in the distillation flask, which is not volatile with water-vapour, and which after recrystallisation from hot water melts at 132—132.5°.

Properties of the pyrridyl-pyrrole melting at 90°.

This substance is obtained from benzene, to which some ligroine has been added, in hard, very shiny, colourless octohedrical crystals. We found 19,41 % for the nitrogen content; 19,44 % was calculated for $C_9H_8N_2$.

This substance is readily soluble in alcohol, ether, chloroform acetone and benzene; less easily in hot water and ligroine, very little in petroleum ether. These solutions exhibit a blue fluorescence, except the aqueous and alcoholic solution. A solution of β-pyridyl α-pyrrole also shows fluorescence according to PICTET and CRÉPIEUX.

Our pyrrole derivative does not give a colour reaction with a pine-chip moistened with hydrochloric acid; with a hydrochloric acid

solution of dimethyl-aminobenzaldehyde there appears, however, a red-violet colour.

Metallic potassium acts on this substance: a potassium compound is formed, as is to be expected. For this purpose we dissolved the substance in toluene, and let the potassium act at the boiling temperature of the solution. At first the action proceeds pretty rapidly, but it soon slows down, so that the heating must be prolonged. The potassium compound was deposited as an insoluble yellow-brown powder.

In order to ascertain the structure of the C-(α-pyridyl)-pyrrole, we have oxidized two grammes of this substance with potassium permanganate in sulphuric acid solution. The oxidation takes place very readily at the ordinary temperature. Out of the reaction product we have isolated the characteristic violet copper salt of picolinic acid, and from this salt we freed the picolinic acid itself by addition of sulphuretted hydrogen. The picolinic acid thus obtained was sublimated in order to purify it. The sublimated preparation melted at 134°.2, while we found 136°.8 for the melting-point of picolinic acid obtained by oxidation of picoline. The melting-point of the mixture of these two preparations was 132.5°—133°. The nitrogen percentage of our preparation that melted at 134.2, was 11.25 % (calculated for picolinic acid 11.38 %). In spite of the slightly too low melting-point there is no doubt of the identity of our preparation; the characteristically crystallizing platinum salt had exactly the same appearance as the platinum salt of the picolinic acid prepared from picoline. It appears from this that in the pyrrole derivative melting at 90° the pyrrole nucleus is united to the α-C-atom of the pyridine nucleus.

We have prepared a picrate from this pyridyl pyrrole, which was obtained after recrystallisation from alcohol as fine, yellow needles of the melting-point 227—228°.

We have prepared the iodine methylate of the pyridyl pyrrole melting at 90° by heating this pyrrole derivative in methyl alcoholic solution with an excess of methyl iodide at 100° for three hours. After evaporation of the solvent and of the superfluous methyl iodide the reaction product was recrystallized from methyl alcohol; in this way yellow-brown hard prism-shaped crystals were obtained, which melt at 148°. We found 9,6 % for the nitrogen content, and 44.7 % for the iodine content. The calculated values for $C_{10}H_{11}N_2J$ are N: 9,73 %; J: 44,37 %. This substance has, therefore, been formed by the addition of one molecule of methyl iodide; the group CH_3J is combined with the nitrogen atom of the pyridine nucleus.

Properties of the pyridyl-pyrrole melting at 132° 5.

This substance, which as we already remarked, is not volatile with water vapour, and is separated in this way from the isomer melting at 90°, crystallizes from alcohol or benzene in leaves joined to rosettes; from hot water long needles are obtained.

This base is readily soluble in alcohol, ether, acetone, chloroform, and benzene; not so easily in ligroine and hot water, very little soluble in low-boiling petroleum ether. As far as the solubility properties are concerned, there is, therefore, a close agreement with the isomer melting at 90°. The ethereal solution shows a blue fluorescence.

We found 19,34 % and 19,62 % for the nitrogen content (calculated for $C_9H_8N_2$: 19,44 % N). This base does not give a colour reaction with a pine-chip moistened with hydrochloric acid; with a hydrochloric acid solution of dimethylamino-benzaldehyde there appears, however, a cherry-red colour, which has changed into blueviolet after a day.

That this substance, too, possesses a pyrrole nucleus, appears again from the behaviour towards metallic potassium. The base was dissolved in toluene and the calculated quantity of potassium was added. The potassium dissolves with vigorous generation of hydrogen; the reaction is much more rapid than with the isomer of melting-point of 90°. The potassium compound is deposited as a white powder.

We have oxidized the pyridyl pyrrole of melting-point 132.5 in the same way with potassium permanganate in an acid solution, as we already described for the isomer of melting-point of 90°. From the pyridyl pyrrole melting at 132°.5 we likewise obtained picolinic acid, which melted at 136°.8 after sublimation, and was identical with the picolinic acid from picoline.

It results from these experiments that the two substances that are formed from N-(*α*-pyridyl)-pyrrole, are two isomeric C-(*α*-pyridyl)-pyrroles, which are distinguished in this that the pyrrole-nucleus in one substance is substituted at the *α*-place, and in the other substance at the *β*-place, as is expressed in formulae (VI) and (VII).

We may also mention that in this reaction chiefly the isomer melting at 90° is formed; the quantity of the isomer melting at 132°.5 is small.

§ 4. *The methylation of the C-(α-pyridyl)-pyrole of melting-point* 90°.

The next step in the synthesis of a substance isomeric with nicotine is that the hydrogen atom of the imide group of the pyrrole-nucleus is replaced by the methyl rest.

The difficulties experienced by PICTET and CRÉPIEUX when they endeavoured to realize the reaction, were already pointed out in the introduction. We met with the same difficulties in our case. The potassium compound of the pyridyl pyrrole melting at 90° was heated with an excess of methyl iodide in a sealed tube at 100° for three hours. The reaction product was freed from superfluous excess of methyl iodide and solved in water. On evaporation of the aqueous solution crystals were separated, while potassium iodide was present in the mother liquor. These crystals were purified by recrystallisation from a small quantity of water. Yellow-brown crystals were obtained, melting at 186°. Analysis gave 8.95 for the nitrogen percentage, and 42,55 for the iodine percentage. Calculated for $C_{11}H_{13}N_2I$: Nitrogen 9,34 %, iodine 42.30 %.

This substance is, therefore, the iodine methylate of C (α-pyridyl)-N-methyl-pyrrole: $(CH_3I)\,N{-}C_5H_4\,.\,C_4H_3N\,.\,CH_3$.

Just as in PICTET and CRÉPIEUX' experiments not only was the nitrogen atom of the pyrrole nucleus methylated, but also a molecule of methyl iodide had combined with the nitrogen atom of the pyridine-nucleus.

This iodine methylate is easily soluble in water, sparingly in alcohol, very little soluble in the other usual organic solvents.

In order to split off the group CH_3I out of this compound, we have followed the method which PICTET and ROTSCHY [1]) already applied, i.e. heating with quick lime.

The jodine-methylate was mixed with quick lime, and slowly heated in a retort. Soon a liquid distilled over, which was received in ether, in order to separate it from a little of the unchanged methyl iodide compound, which had also been distilled over in a small quantity. After evaporation of the ethereal solution there was left a light yellow liquid; we have converted this base into the picrate, which melted at 143° after a double recrystallisation from alcohol. We found 18.19 for the nitrogen percentage of this substance, while 18.09 % of nitrogen is calculated for the monopicrate of C (α-pyridyl)-N-methyl-pyrrole,

We have, accordingly, very probably obtained the required methyl derivative, which must, therefore, be an isomer of nicotyrine.

It seems, however, possible to carry out the methylation of the C (α-pyridyl) pyrrole in such a way that the C (α-pyridyl) N-methyl-pyrrole is obtained without the necessity of following the indirect way over the iodine methylate.

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[1]) L. c.

It had, indeed, already appeared that the addition of methyl iodide to the pyridyl pyrrole of melting point 90° only takes place at a higher temperature, whereas PICTET and CRÉPIEUX' pyridyl pyrrole combines with methyl iodide already at the ordinary temperature.

For this reason we have heated a mixture of pyridyl pyrrole potassium with methyl iodide in molecular quantities in a sealed tube at 50°. The reaction mixture was a solid mass, in which pyridyl pyrrole potassium and the above mentioned methyl iodide compound of C-(pyridyl)-N-methyl-pyrrole were present. It was, however, possible to extract by means of ether a little of a yellow oil from this reaction mixture. This liquid was received in alcohol, and picric acid was added; a picrate crystallized out, which melted at 142° when it had been recrystallized out of alcohol, and appeared to be identical with the picrate of the C (α-pyridyl)-N-methyl-pyrrole described above, as appeared from the melting point of the mixture of both preparations.

We shall first of all set ourselves the task of preparing a larger quantity of this C(α-pyridyl)-N-methyl-pyrrole, and examining its properties closely. We shall further try to determine the structure of the two isomeric pyridyl pyrroles more exactly.

A full communication of this investigation will appear in the Recueil des Travaux chimiques des Pays Bas.

Organic-chemical Laboratory of the University.

Amsterdam, March 1923.

Bacteriology. — "*The splitting of lipoids by Bacteria.*" (First communication.) By G. M. KRAAY and L. K. WOLFF. (Communicated by Prof. C. EYKMAN.)

(Communicated at the meeting of June 30, 1923).

The splitting of fats by bacteria has often been investigated and the behaviour of the lipases has properly been recorded. However no literature dealing with the splitting of lipoides by *bacteria* is known to us. Also in general physiological chemistry little information is given concerning the splitting of lipoids (lecithin) by enzymes, apart from the beautiful researches by DELEZENNE and FOURNEAU about the splitting of lecithin by serpent venom. In many respects we thought it of interest to investigate the action of bacteria on lipoids, the formation of strong blood poisons being possible, as DELEZENNE and FOURNEAU found as the result of the action of serpent venom on lecithin. We first tried to find out whether some fat-splitting bacteria are able to split lecithin and further if there exist among the non-fat-splitters some that will split lecithin.

Considering our working method this; we mostly used plates with lecithin agar obtained by shaking up a small quantity of lecithin and ordinary nutrient agar (about 0.5 gram per 100 gr.) at about 50° C. If the lecithin is affected an area is formed all around the streeks of inoculation.

It appears on microscopical examination that this area contains per surface unit more grains than are to by found anywhere else in the culture medium. Plates with yolk of egg cannot be used; the fat contents of yolk of egg cannot be used; the fat contents of yolk of egg makes one unable to distinguish lecithin-splitters from fat-splitters. Our results are summarized in the following table. Our conclusions based upon this table are: there exists fat-splitting bacteria unable to affect lecithin; lecithin-splitting bacteria unable to act upon fat, bacteria unable to act upon both fat and lecithin, and bacteria able to act upon both. (See table on p. 437).

The latter bacillus, a very strong lecithin splitter, but quite unable to split fat has been isolated by us from brackish water; this bacillus resembles much the bac. piscium pyogenes described by MATZUSCHITA.

	Splitting of	
	fat	lecithin
bact. typhi	—	—
„ coli	—	—
„ dysenteriae Shiga	—	—
„ prodigiosus	+	+
„ pyocyaneus	+	+
„ fluor. liquef.	+	+
„ proteus[1])	—	—
staphylocc. pyogenes	+	—
spir. El Tor.	—	+
„ Dunbar	—	+
„ Cholerae	—	—
Bac. piscium pyogenes?	—	+

We have not yet resolved the question, how the lecithin is broken down; we can only say that as a result of the splitting by the here above mentioned bacteria no hemolysines are formed. We could not find a link between hemolysis by bacteria and lipolysis or lipoidolysis; we found a staphylocc. which had lost its hemolytic property but not its lipolytic character and on the other hand one of our colistrains behaved hemolytic but was inactive on fat or lecithin, our bac. piscium pyogenes splitted lecithin but had no hemolytic action.

No fatty acids could be titrated in broth containing splitted lecithin (B. piscium prog.). This result is in agreement with observations on the non-hemolytic action of the splitted lecithin, because if lecithin is splitted in such a manner that (unsaturated) fatty acids are formed, a hemolytic action must take place.

We still want to mention that the power of splitting of the bacteria in the table, has been tried on cholesterol and lanoline, the latter was affected only by a staph. pyog., the former only by B. pyocyaneus.

June 1923. *Laboratory of hygiene of the University of Amsterdam.*

[1]) One of our proteus strains affected fat.

Physiology. — *"The Presence of Cardio-regulative Nerves in Petromyzon fluviatilis"*. By J. B. ZWAARDEMAKER. (Communicated by Prof. H. ZWAARDEMAKER.)

(Communicated at the meeting of March 24, 1923).

In the 2nd edition of his "Physiologie des Kreislaufs" TIGERSTEDT [1]) remarks that inhibitory cardiac nerves are present in nearly all vertebrates. Only among the cyclostomata some exceptions are known. GREENE [2]) found that in Myxine electrical stimulation, starting from the brain, the spinal cord or the vagi did not affect the frequency of the heart-beat. CARLSON [3]) corroborated this finding and tried to extend the investigation to another group of cyclostomata, viz. the petromyzonta. At first he could work only on the larval form, in which cardio-regulative nerves appeared to be absent. Afterwards he examined adult animals [4]). When, in these experiments, he applied an electrical stimulus to the medulla oblongata on the level of the vagus nucleus, he noted a brief standstill, which was followed by an accelerated rhythm. From this he concludes that "the central nervous system is connected with the heart by ordinary augmentor and probably also by inhibitory nerves" (l. c. p. 231).

In the continuing volume of his "Vergleichende Anatomie der Myxinoiden" JOHANNES MÜLLER makes mention of a connection between. N. sympathicus and cardiac nerves [5]). He also adds some remarks about the N. vagus, for which I think it better to refer to the original work (l. c. p. 59 sqq.)

The first experiments which I made myself to ascertain whether in petromyzon fluviatilis any influence is exerted by the central nervous system upon the heart's action, yielded a negative result, which was in accordance with GREENE and with the first set of experiments performed by CARLSON [6]). However, I have been in a position to extend my research. In order to preclude

[1]) R. TIGERSTEDT, Die Physiologie des Kreislaufs II p. 319.

[2]) CH. W. GREENE, Amer. Journ. of Physiol. VI p. 318 1901.

[3]) A. J. CARLSON, Zeitschr. f. allg. Physiol. IV p. 259 1904.

[4]) A. J. CARLSON, Amer. Journ. of Physiol. XVI p. 230 1906.

[5]) J. MÜLLER, Fortsetzung der vergleichenden Anatomie der Myxinoiden p. 57. Berlin 1838.

[6]) J. B. ZWAARDEMAKER, Physiologendag Amsterdam Dec. 1922.

movements of the animal I curarized it beforehand. Paralysis of the skeletal muscles can, in fishes, be effected only with very large doses [1]). For my animals I used 4 mgr. tubo curari of which, 2 mgr., injected intraperitoneally, was sufficient to paralyze a 220 gr.-rat. after 7 minutes. This also plays an influence upon the vagus-function [2]), but this inconvenience could readily be obviated by the technique followed, because the synapses of the vagus are restored sooner than the motor innervation.

After the injection the animal was let alone until no "Stellreflexe" were distinguishable any longer. Also the gills are completely motionless then. At that juncture the cerebrum is severed from the rest of the nervous system by an incision posteriorly along the eyes. After this the cerebrum and the spinal cord are laid bare down to the second gill-hole. Now a straight glass cannula is inserted into the Vena cava dextra, through which the animal, in ventral position, is perfused during some time with RINGER's fluid, containing $6^1/_2$ gr. NaCl, 200 mgr. $NaHCO_3$, 200 mgr. $CaCl_2$, 200 mgr. KCl [3]). The surplus of curari is hereby gradually washed out. Through a window in the cartilagenous pericardium [4]) the atrium is fixed to a lever beneath the animal. Now two thin platinum electrodes are fixed, so as to be well visible, at the level where stimulation produces the effect aimed at. With strongly curarized animals it sometimes takes rather a long time before any effect can be distinguished. At that moment, however, the animal is perfectly quiet, and the experimenter can be sure that only the movements of the heart are registered. In subsequent periods of the perfusion also the contraction of the gills can be distinguished. The electrodes are connected with the secondary coil of an inductorium of DUBOIS-REYMOND, provided with a NEEF-hammer. An accumulator is connected up in the

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[1]) *a.* J. SCHIFFER, Arch. f. Anat. u. Physiol. p. 453, 1868.
b. J. STEINER, ibid 1875.
c. BOLL, Mon. Ber. d. Kgl. Preuss. Akad. d. Wissensch. Nov. 1875.
d. J. STEINER, Das americanische Pfeilgift Curare p. 56.
c. and *d.* After R. BOEHM's article in Handbuch der experimentellen Pharmacologie II 1. Hälfte p. 183.

[2]) R. BOEHM, l. c. p. 202

[3]) J. B. ZWAARDEMAKER, Diss. Utrecht 1922.

[4]) When the pericardium is being opened it all at once changes colour. Originally the heart is seen to loom vaguely through the transparent cartilaginous tissue with a bluish tint; after the opening the pericardium shows its own milkwhite colour, while the atrium now appears to lie at tbe bottom of the cavity. Apparently in the pericardium a negative pressure obtains, which of course is lost at the opening, so that the atrium partly collapses.

primary circuit. The Pfeilsignal, which was used sometimes (e.g. in the first figure), could not be placed in shunt, so it came in the primary circuit. The obtained coil-distances (C. d.) are smaller than when no signal is connected up. On stimulation we note a considerable acceleration shortly after the stimulus has been set up. If the stimulus continues a short time only (in fig. 1 5 seconds) the acceleration will be seen to disappear soon and to be substituted by a retardation ; in case the latter increases, the heart is brought to a standstill. After cessation of the negative chronotropic effect,

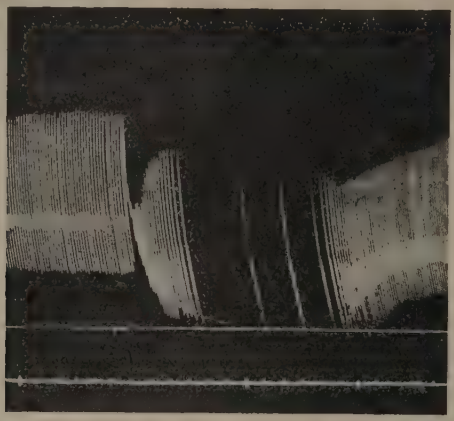


Fig. 1.
Accelerans-vagus effect.
Petromyzon fluviatilis. Perfused with RINGER's mixture. Stimulation for 5 seconds of medulla oblongata of the level of the exit of the N. vagus. C. d. 100.
The tracings from above downward: record of atrium movement
" " stimulus signal
" " time line 10 sec.

a new rhythm appears, more rapid than the original. A little later it gives way to the old rhythm. In fig. 1 the rhythm prior to the stimulation is ± 45 beats per minute, after the standstill the frequency amounts to 55. The action of side-currents upon the heartmuscle need not be taken into consideration in these experiments, because the effect appears only when a sharply defined area in the medulla oblongata is stimulated and the effect is destroyed again by a slight displacement of the electrodes. Besides this a great influence is exerted by summation. A stimulus, for instance, that produces no effect after 5 seconds, causes a distinct standstill after a longer period.

When instead of presenting a short stimulus, the current is sent through permanently, at first a marked quickening of the rhythm will be noted, attended with a marked positive inotropic effect. This is apparently an accelerans effect.

Fig. 2.

Petromyzon fluviatilis.

Fatigue of accelerans and vagus through permanent stimulation from medulla oblongata. The stimulus starts at the first elevations. C. d. 143. This continues as far as the stroke. Time 10 sec.

When breaking the current during this period a standstill will rapidly ensue, which will disappear again directly after fresh stimulation. When, however, the current passes continuously, a slower rhythm will appear after some time spontaneously (in fig. 2 ± 30 seconds), while at the same time the height of the contractions diminishes gradually. It is the transition to a distinct vagus-effect. When this rhythm has also continued for some time (in fig. 2 about 1 min.), it will change into a rhythm that is only slightly quicker than the normal, or does not differ from it at all, and will persist unaltered after the breaking of the current.

When perfusing the animal with a potassium-free uranium-containing, instead of a potassium-containing fluid we shall see that the phenomena are practically the same in the K-, and in the U-condition. First we see an acceleration, then a retardation, which in some cases is followed again by an acceleration. This, however, is never so pronounced as at the beginning of the stimulation.

What has been said above goes to show that:

1. in Petromyzon fluviatilis cardio-regulative nerves are present.

2. with the technique employed after the removal of curari the excitability of the cardiac nerves returns sooner than that of the motor nerves.

3. in the curarized animal the latent period of the accelerans is shorter than that of the vagus.

4. with long-continued stimulation the accelerans-effect is noticeable before the vagus-effect.

5. with brief stimulation the vagus effect appears only after cessation of the stimulation.

6. after cessation of the vagus-action an acceleration will sometimes follow, which is perhaps due to a longer after-effect of the accelerans-stimulation.

Chemistry. — "*The Light Oxidation of Alcohol* (III). *The Photo-Catalytic Influence of some Series of Ketones on the light Oxidation of Ethyl Alcohol*". By W. D. COHEN. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of May 26, 1923).

Introduction. A first communication on this subject appeared in these proceedings [1]) already several years ago; a continuation of this was published by BÖESEKEN [2]). In this paper the theoretical grounds on which these researches are founded, are set forth in extenso [3]), and we may, therefore, refer to this treatise for a study of them.

It was now my purpose to examine what relation exists between the configuration of a ketone and its photo-catalytic influence on the oxidation of a definite alcohol, and for this reason I studied the influence of some series of ketones on the velocity of oxidation of ethyl alcohol, to be able, if possible to arrive at a conclusion with regard to the constitutive requirements which a ketone must satisfy to be able to act as a photo-catalyst under the circumstances specified later, which at the same time establishes its photo-chemical attackability. This question has, indeed, already been mentioned more than once before [4]), but the comparatively small regularity in the observed phenomena rendered an extension of the research in this direction very desirable.

The light-thermostat. In the reaction:

Light + Ketone + Alcohol + Oxygen = Ketone + Aldehyde + Water

a certain quantity of oxygen disappears, and the rapidity with which the oxygen is absorbed, is under for the rest fixed circumstances, a measure for the photo-catalytic activity of the examined ketone.

The light thermostat (fig. 1) consists of a copper trough, provided with two windows placed opposite each other in the longitudinal walls, which make a continual observation of the reaction vessel

1) BÖESEKEN and COHEN, These Proc. XVIII, p. 1640.
2) BÖESEKEN, Rec. 40, 433 (1921).
3) Ibid, 437.
4) COHEN, Rec. 39, 258 (1920). Chem. Weekblad 13, 902 (1916).

possible, and a window in the bottom for the illumination. The thermostat rests on an iron framework, which has become an entirely

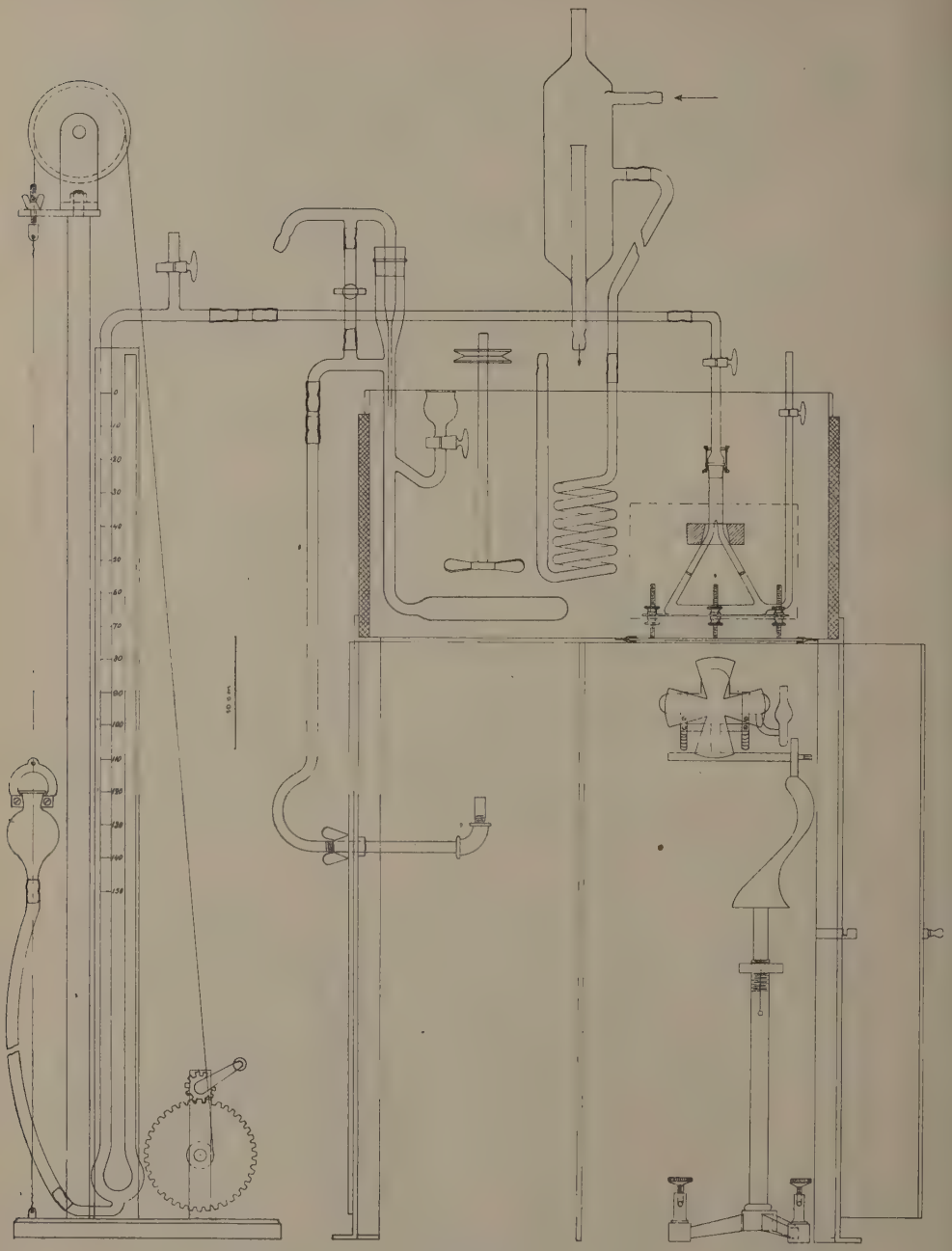


Fig. 1.

closed space by a cover of incombustible material. This space is divided in two by a vertical partition. On the left there are found two gas-burners connected with a thermo-regulator, and on the right there is adjusted a Heraeus quartz lamp. To work this the wall in the lefthand side of the framework is made like a door (drawn halfopen in the figure); in the front partition at the place of the incandescent body there is a ventilator which works by suction and serves to cool the lamp. The water in the thermostat can further be cooled by means of a cooling spiral, through which water flows under constant pressure, a screw stirrer ensuring thorough mixing in the trough; besides the windows, the vertical walls are insulated with felt. Ventilator and stirring apparatus are worked by separate regulatable motors. The temperature of the thermostat can be kept constant at $35 + {}^{1}/_{100}{}^{\circ}$, which temperature has been chosen, because at this temperature the thermostat can be regulated most accurately.

As reaction vessel I, at first, used the before described stirring-apparatus [1]) (fig. 2); it possesses the drawback, however, that the surface of illumination is small, the accuracy of the measurement being seriously impaired by the rapid contamination of the mercury in the mercury feal. Therefore I tried to modify the reaction vessel in such a way that also without intensive mixing of gas and liquid, an alcoholic liquid could be obtained, which remains saturated with oxygen, or contains at least such an excess of oxygen that there can be no question of measuring a velocity of diffusion instead of a velocity of reaction.

This is possible when the thickness of the liquid layer is taken very small (about 1 mm.). According to fig. 3 a reaction vessel is then obtained, which chiefly consists of a flask with a perfectly flat bottom; the dimensions being such that 5 cc. of liquid give a thickness of layer of 5 mm. The neck is narrow and possesses a ground piece to which a bent capillary tube with tap can be attached. Near the bottom there is further a side tube with tap, through which the whole apparatus can be filled with oxygen. Besides there is a filling body in the flask, to make the gas-volume as small as possible in proportion to the surface of illumination; this considerably enhances the accuracy of the measurement. For definite purposes this filling body has been made to a second reaction vessel within the former; then an apparatus is obtained as is shown in fig. 4.

By the aid of a narrow tube the reaction vessel is connected with the micromanometer. The lefthand leg of this has a capacity

[1]) These Proc. XVIII, p. 1642.

of 1,5 cc. and is divided into 150 parts. Each space between two dividing lines represents, therefore, a capacity of 0.01 cc. The adjustment is obtained by moving the flask up and down by means of a hoisting apparatus, the position of the meniscus in the two

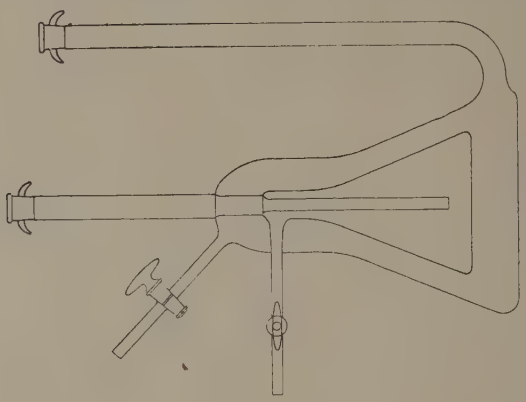


Fig. 5.

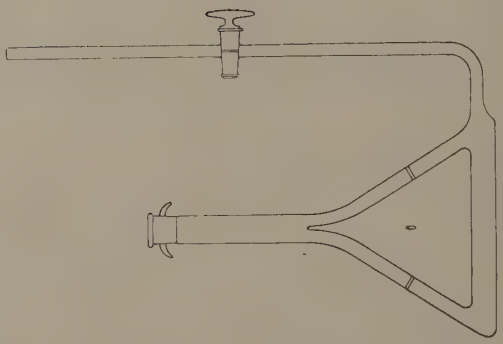


Fig. 3.

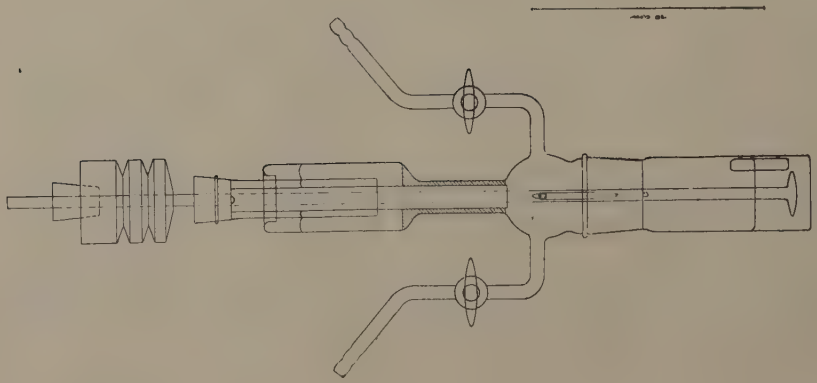


Fig 2.

legs of the manometer being verified by a mirror behind it, on which horizontal lines are drawn at distances of 1 mm. When the apparatus has been properly cleaned and filled with distilled mercury, an accuracy of adjustment can be attained of 1 or 2 hundredths, which as well as the influence of the temperature lies within the limits of the error of observation. The calibration error of the apparatus was so small that it could be neglected.

After having been weighted with a copper ring, the reaction vessel is placed on a glass table, which itself rests on the bottom plate of the thermostat. The table can be put in a horizontal position by means of three adjusting screws, through which the thin liquid layer entirely covers the bottom surface of the reaction vessel. After being lit the incandescent body of the lamp is always placed in a horizontal position; the lamp burns at a terminal voltage of 110 Volts and a series resistance of about 20 Ω constant at 2,7 Amp./40 Volt. Lamp and reaction vessel are always at the same distance from each other; in my experiments the distance from the bottom side of the reaction vessel to the window was 20 mm., and from the upper side of the lamp to the window 25 mm.; taking into account the thickness of the glass, the mutual distance from lamp to object was about 50 mm.

The measurements.

a. The preparations. They were prepared for the greater part by myself or under my supervision, and purified as carefully as possible. As the way of preparing is known for all of them, we may refer for this to the records of the literature published on this subject. When it was possible, at least two preparations of different origin were examined, or the preparation was again recrystallized or distilled after the measurement; the values found were not considered as definitive until they were perfectly constant and reproducible; save for a single exception this was always the case.

b. As solvent, resp. liquid that is to be oxidized, was used absolute ethylalcohol, not because its being absolute was quite indispensable for the success of the reaction — for water is formed during the reaction — but in order to start always from a solution of constant proporties. In my earlier investigations I had come to the conclusion that water would be a strong anti-catalyst, at least for the photo-chemical reduction [1]). At the time I did not yet know the photo-catalytic alcohol oxidation by molecular oxygen, nor that

[1]) Cohen Rec. 39, 244 (1920).

this reaction and the keton reduction were primarily the same, and that it is, therefore, illogical to assume that water would be an anti-catalyst in the ketone reduction. It has really appeared in a new investigation, that there would be no question at least of a considerable anti-catalytic action of water, but that the error made before, which has, unfortunately, already been adopted in the handbooks [1]), must be attributed to a wrong interpretation of the experiments made at the time.

It seems to me of use to discuss this a little more at length, if it were only to point out how easily certain phenomena are overlooked in the study of a reaction. For at first I made my experiments on the photochemical ketone reduction in such a way that I illuminated the 96 % alcoholic solution in a thin layer in *open* flasks, but did not observe then anything of the crystallisation of the sparingly soluble pinacone already described by CIAMICIAN [2]). This succeeded however without any difficulty when I used absolute alcohol — as CIAMICIAN also did —, and besides worked in *closed* apparatus, hence with exclusion of oxygen. I then drew the very plausible conclusion, which proved erroneous afterwards, that water would be a strong anti-catalyst, and quite overlooked the interesting photo-catalytic alcohol oxidation in which — the results of this paper are a convincing proof of this — aldehyde *does* appear, but no pinacone [3]), and which was not discovered until a few years later.

c. In order to be able always to have a great excess of oxygen at our disposal, the reaction vessel after addition of 5 cc. of the solution to be examined, is filled with oxygen which is saturated with alcohol vapour in a washing bottle. Under these circumstances the solution always remains more than sufficiently saturated with oxygen; it is, however, without influence on the result of the measurements, if the gas in the reaction vessel is air or oxygen; for the sake of safety oxygen was, however, always taken.

The measurements, the results of which are combined in the following table, extend chiefly over the following series of ketones:

a. benzophenon and its hydration products in the nucleus,

b. acetophenon and some alkyl-, and also phenyl substitution products in the CH_3-group,

c. the phenyl substitution products of acetone,

d. the simplest aliphatic, aromatic, and fat aromatic α-β-diketones,

e. some α-β-γ-triketones.

The figures over the horizontal division line indicate the molar

[1]) HOUBEN—WEYL. Die Methoden der organischen Chemie 2te Aufl. (1922), Band II pag. 983.

[2]) CIAMICIAN and SILBER, Ber. 33 2911 (1900); 34 1530 (1901); 44 1288 (1911).

[3]) BÖESEKEN and COHEN, l.c.

concentration of the ketone, the values under it representing the oxygen absorption, expressed in cc. per hour. They are the mean of a great many mutually concordant observations.

1. Benzophenon.

1 (saturated)	3/4	1/2	1/4	1/8	1/16	1/32	1/64
10.30	**12.00**	**12.00**	**11.90**	**9.00**	5.60	3.65	2.28

2. Phenylcyclohexylketone.

1 (saturated)	1/2	1/4	1/8
5.15	**5.00**	2.82	1.12

3. Dicyclohexylketone. Inactive in all concentrations.

4. Phenyl n. hexylketone.

2	1	1/2	1/4
1.00	**0.97**	0.68	0.22

5. Di-n hexylketone. Inactive in all concentrations.

6. Acetophenon.

2	1 1/2	1	1/2	1/4
1.30	**1.40**	**1.42**	1.03	0.22

7. Propiophenon.

2	1	1/2	1/4
1.10	**1.11**	0.92	0.20

8 Phenylbenzylketone.

1/2 (saturated)	1/4	1/8
5.05	**4.85**	2.35

9. Diphenylacetophenon.

1/32 (saturated)	1/64
3.13	0.78

10. Triphenylacetophenon (β-benzpinacoline). Inactive.

11. Acetone. Inactive in all concentrations.

12. Monophenylacetone.

3	2	1
0.50	**0.48**	0.35

13. Symm Diphenylacetone (dibenzylketone).

2	1	1/2
1.76	1.75	0.85

14. Asymm. Diphenylacetone.

1 (saturated)	1/2
0.03	0.01

15. Triphenylacetone 1.1.2.

1/8 (saturated)
0.05

16. Symm Tetraphenylacetone [1]).

1/50 (saturated)
0.17

17. Phenylfurylketone.

2	1	1/2
0.07	0.10	0.10

18. Diacetyl.

4	3	2	1 1/2	1	3/4	1/2	1/4	1/8	1/16	1/32
16.00	15.30	15.30	15.10	14.90	14.10	10.60	6.40	2.60	0.64	0.16

19. Benzil.

1/4 (saturated)	1/8	1/16
3.20	1.44	0.52

20. Acetylbenzoyl [2]).

4	3 1/2	3	2	1 1/2	1	3/4	1/2	1/4	1/8	1/16
8.60	11.70	12.90	12.60	12.80	13.10	10.80	8.50	6.05	4.15	2.08

[1]) Prof. STAUDINGER, Zürich, had the kindness to send me a small quantity of this preparation.

[2]) By illuminating an alcoholic solution of acetylbenzoyl in a sealed tube the corresponding photoreduction product can be very easily obtained. The substance consists of very fine colourless crystal needles, sparingly soluble in alcohol, and is perfectly stable at the air in dry condition. For the rest the compound is quite comparable with the corresponding reduction product of diacetyl (Comp. Chem.

21. Furil.

1/16 (saturated)
2.80

Remark. After some time's illumination the absorption, which was constant at first, descends to 0; in this the ketone itself is attacked with decoloration of the liquid

22. Benzfuril.

2	1	1/2	1/16
5.80	6.30	6.20	2.20

23. Terephtalophenon.

0.01 (saturated)	0.006	0.004
2.80	3.55	3.45

24. Isophtalophenon.

0.1 (saturated)	0.01
2.80	1.48

25. Phenanthrenequinone

0.02 (saturated)	0.01
10.50	6.25

Remark. Behaves like furil.

26. Anthraquinone.

0.004 (saturated)
0.67

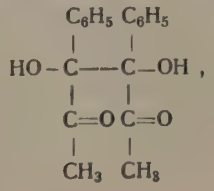
27. Camphorquinone. The activity varies with the origin of the preparations. Some five varied at 1/8 mol. from 0.19—0.43. With still lower concentrations, and also with very small ones the activity is practically not perceptible

28. Fluorenone. In all concentrations — also very small ones — inactive.

29. α-Hydrindon.

2	1	1/2
0.19	0.17	0.07

Weekbl. 13, 594 (1916); it melts amidst decomposition at 116°—124°. It is still uncertain whether the structure formula is:



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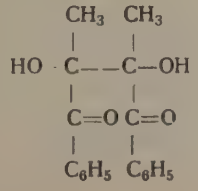


30. β-Hydrindon. Is useless as a photocatalyst, as this substance itself is very readily attacked by oxygen in alcoholic solution.

31. Indanedion 1.2.

1/8 (saturated)	1/16
0.92	0.39

32. Pentanetriketone. Inactive.

33. Diphenyltriketone. Inactive.

34. Alloxane. Exceedingly slight activity.

These data allow us to draw the following conclusions:

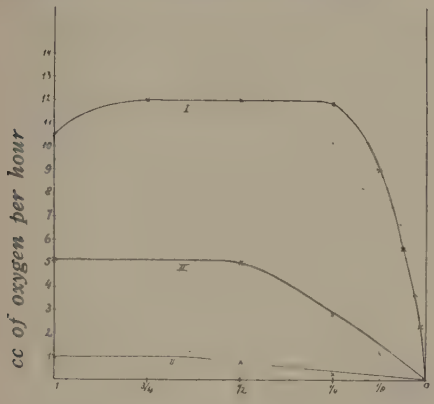
a. The velocities of activation are independent of the concentration of the ketone (printed in bold type in the tables) within comparatively wide limits, quite corresponding to the reduction velocities found before[1]). This phenomenon does not, indeed, manifest itself in all the examined cases, but it should not be forgotten that the circumstances of the experiment necessitate a certain degree of activity and solubility of the ketone to reach the maximum velocity of activation.

Clear examples in which the oxygen absorption remains constant within wide limits, are benzophenon, diacetyl, and benzoyl acetyl (compare the graphical representations in fig. 5 and 6). We sometimes see the activity diminish again in very high ketone concentrations (20) or in the neighbourhood of the point of saturation (1), which must then be attributed to mutual disturbances of the ketone molecules[2]). The diminution of activity in lower concentrations must simply be accounted for by the absence of a sufficient quantity of activable ketone molecules, in which part of the available light is left unused. That really in the concentration region of the maximum activation all the photo-active light is absorbed by a layer only 1 mm. thick, I have been able to prove very clearly by means of the reaction vessel according to fig. 4, which can, therefore, be perfectly compared with the "mantle tubes" described formerly for the photo-chemical reduction. When e.g. an alcoholic (or a benzolic) solution of benzophenon in a concentration necessary for the maximum activation is brought into the outer reaction vessel, a benzophenon solution in the inner reaction vessel appears to absorb no trace of oxygen; the absorption begins, however, to become immediately perceptible, as soon as the ketone concentration in the outer

[1]) Cohen, Rec. 39, 253 (1920).

[2]) Ibid. p. 273.

vessel descends below the critical. In the region of maximum activation all the photo active light is, therefore, arrested by a layer of 1 mm., and this takes place independent of the solvent used. These phenomena are in perfect harmony with what was found before in the ketone reduction. Corresponding experiments with diacetyl and benzoyl acetyl lead to perfectly the same results.



I. benzophenon
II. phenylcyclohexyl ketone } Fig. 5.
III. phenyl. n. hexyl ketone

III. „ „ „
IV. acetophenon
V. acetylbenzoyl } Fig. 6.
VI. diacetyl

Fig. 5.

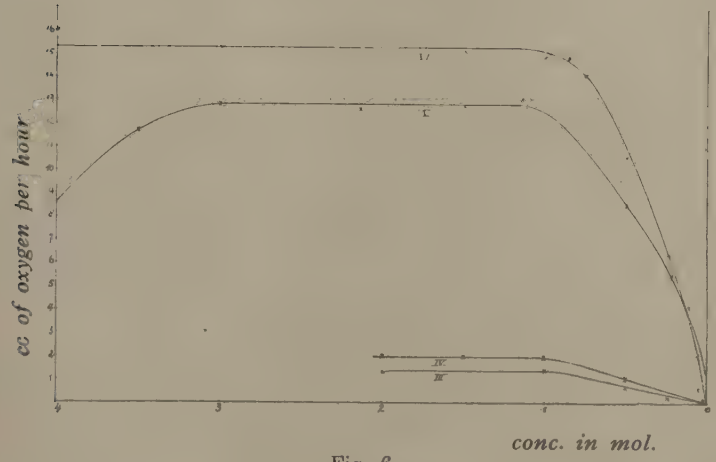


Fig. 6.

b. For the photo-activity of the mono-ketones the "aromatic", character is in general decisive [1]), constitutive factors being of influence by the side of it. Thus the photo-activity of benzophenon has been reduced to about half its value, when one of the nuclei

[1]) Cohen, Chem. Weekbl. 13, 902 (1916).

has been hydrated (2) (fig. 5), and it has quite disappeared in the dicyclohexyl ketone (3). That for the rest the cyclohexyl nucleus weakens the activity of the phenyl nucleus less than a purely aliphatic group, is proved by the much smaller activity of phenyl n. hexyl ketone (4) (fig. 5), which may be put on a line with the activity of acetophenon and propiophenon (6,7) (fig. 6). On introduction of C_6H_5-groups into the CH_3-group of acetophenon, the activity at first greatly increases (8,9), suddenly becoming 0 in triphenyl acetone. It is, indeed, known that β-benzpinacoline lacks all the ketone characteristics. In the phenyl substitution products of acetone (quite inactive in themselves, just as di-n-hexyl keton (5, 11)), the introduction of only one phenyl group appears to make the compound photo-active (12). Of the higher phenyl substitution products, the molecules built symmetrically show the greatest activity (compare 13 and 16 with 14 and 15).

c. The photo-activity of the α-β-di ketones is a much more general property, and bound neither to the specifically aliphatic or aromatic character, nor in particular to the more or less symmetrical structure of the molecule. The introduction of a second $C=O$ group has mostly a greatly strengthening influence on the photo-activity (compare 18 and 20 with 11 and 6), in which possible disturbing influences issuing from the rest of the molecule, are thrown into the background. In this connection it is e. g. interesting to point out that phenanthrene quinone (25), which is to be considered as a particularly ortho-substituted benzil, far exceeds all the examined ketones with regard to its relative activity, whereas fluorenon (28), which may be compared with it, is perfectly inactive. The opposite case presents itself in the comparison of benzil (19) with regard to benzophenon (1), where the di-ketone compared with the mono-ketone is less active. It may, however, be possible that in consequence of the slight solubility of benzil in alcohol the maximum activation concentration cannot be reached.

Of great importance is also the activity of the α-β-di-ketones, which carry one or two furane-nuclei (21 and 22), which furnishes a new proof of the great resemblance in properties of the furane and benzol derivatives.

d. Thus we see that the phenyl and furyl groups do not exert a disturbing influence on each other in the α-β-di-ketone; this influence is, however, evidently particularly strong in the corresponding mono-ketone, phenyl furyl ketone (17), which presents a very small activity. Here the above-mentioned influence of the symmetry of the molecule on the photo-activity of the mono-ketone is very

pronounced. This influence of the symmetry was already observed more than once in the photo-chemical reduction of the substitution products of benzophenon, but it had not been recognized as such [1]). To give a further support to this view it has been tried to make di-furyl ketone, as this compound would have to possess an activity equivalent to benzophenon. Unfortunately all attempts to obtain this substance have failed so far [2]), but in this connection attention may already be drawn to the much greater activity of terephtalophenon compared with isophtalophenon (23 and 24).

e. A somewhat separate place among the α-β-diketones occupies camphorquinone, the activity of which is unexpectedly slight, and moreover not reproducible. The greater or smaller purity of the preparations seems to be of great influence.

f. α-Hydrindon (29) and indane dion 1 . 2 . (31), considered as internal condensation products of resp. propiophenon (7) and acetyl benzoyl (20), present a greatly diminished activity. β-Hydrindon cannot be used as object of comparison with mono-phenyl acetone on account of its great oxidisibility.

g. The photo-activity of the examined α-β-γ-tri-ketones is zero, or so small as to be negligible (32, 33, 34) [3]). This phenomenon must, without any doubt, be attributed to the paralysis of the middle C=O group caused by the solvent [4]), through which the compound has practically quite lost its favourable properties of double α-β-diketone. [5])

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Delft, April 1923.

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[1]) Compare. COHEN, Rec. 39, 258 (1920).

[2]) FREUNDLER, Bl. (3) 17, 612 (1897).

[3]) Compare for the photo-chemical reduction of alloxane Ciamician and Silber, Ber. 36, 1581 (1903).

[4]) At first pentane tri-ketone and di-phenyl tri-ketone dissolve in absolute alcohol with a dark yellow colour, after standing some time the colour of the solution changes into light yellow, in which very probably alcohol addition products $CH_3-CO-C\begin{matrix}OH\\ \\ OC_2H_5\end{matrix}-CO-CH_3$ and $C_6H_5-CO-C\begin{matrix}OH\\ \\ OC_2H_5\end{matrix}-CO-C_6H_5$ which are analogous to the hydrate, are formed.

[5]) Comp. SACHS, Ber. 34, 3052 (1901); 35, 3311 (1902); VON PECHMANN, Ber. 23, 3380 (1890); WIELAND, Ber. 37, 1531 (1904); BILTZ. Ber. 45, 3662 (1912).

Mathematics. — "*On Power Series of the Form*: $x^{p_0} - x^{p_1} + x^{p_2} - \ldots$" By M. J. BELINFANTE. (Communicated by Prof. L. E. J. BROUWER.)

(Communicated at the meeting of April 28, 1923).

Introduction.

It is a well-known theorem of FROBENIUS that if Σa_n is summable of order 1, $\left(\text{i.e. if } \lim_{n=\infty} \frac{s_1 + s_2 + \ldots + s_n}{n} = s, \text{ where } s_n = a_1 + a_2 + \ldots + a_n\right)$ then $\lim. \sum_1^\infty a_n x^n = s$, provided x approaches 1 by real values from below (which we denote by $x \to 1$).[1])

Under the same conditions we have:[2])

$$\lim_{x \to 1} \sum_1^\infty a_n x^{p_n} = s$$

provided $p_1 < p_2 < \ldots$ are integers which satisfy the condition:

$$\nu\,(p_\nu - p_{\nu-1}) < p_\nu . k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Some condition of the form (1) is necessary as may be seen from the following example, where our condition is broken and $\sum_1^\infty a_n x^{p_n}$ has no limit as $x \to 1$.[3])

Put $p_\nu = 2^\nu$ and $a_n = (-1)^{n+1}$, then we have:

$$\lim_{n=\infty} \frac{s_1 + s_2 + \ldots s_n}{n} = \tfrac{1}{2}$$

while $\sum_1^\infty a_n x^{p_n} = x - x^2 + x^4 - x^8 + \ldots$ oscillates between limits at least as wide as 0,498 and 0,502, if $x \to 1$[3]).

Thus we are led to the question: what is the connexion between the exponent-series $p_0, p_1, p_2, p_3, \ldots$ and the existence or non-existence of

$$\lim_{x \to 1} (x^{p_0} - x^{p_1} + x^{p_2} - \ldots)$$

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[1]) BROMWICH, Theory of infinite series, p. 312.

[2]) BROMWICH, op. cit., p. 388.

[3]) BROMWICH, op. cit., p. 498 example 30.

HARDY [1]) has investigated several particular exponent-series with particular methods that cannot be applied to other exponent-series, for instance the series of FIBONACCI:

$$1, 2, 3, 5, 8, \ldots$$

The only general result HARDY could reach was the non-existence of a limit if:

$$p_{\nu+1} > k \,.\, \nu \,.\, p_\nu \,.\, log.\, p_\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

but HARDY's example quoted above (where $p_\nu = 2^\nu$), shows the non-existence of a limit notwithstanding the condition (2) is not satisfied.

In the present paper another condition is given (§ 2), with the aid of a theorem of LITTLEWOOD which is treated in § 1.

§ 1.

LITTLEWOOD has proved the following theorem: [2])

Theorem 1. *If* $n a_n < k$, *and* $\lim_{x \to 1} \sum_1^\infty a_n x^n = s$, *then* $\sum_1^\infty a_n$ *converges to* s.

For our purpose we want the following extension which has also been enunciated by LITTLEWOOD: [3])

Theorem 2. *If the mean-values* [4]) *of order* $k-1$ *of* Σa_n *are limited and* $\lim_{x \to 1} \sum_1^\infty a_n x^n = s$, *then* Σa_n *is summable of order* k.

LITTLEWOOD states that the proof of theorem 2 follows the lines of his proof of theorem 1. The latter being rather long and tedious, it seems not without interest to show that theorem 2 is an immediate consequence of theorem 1.

Adopting the notation of our article "*On a Generalisation of* TAUBER's *Theorem concerning Power Series*" [5]), we have the following relations between the mean-values $A_n^{(k)}$ and the functions q_k:

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[1]) Quarterly Journal, vol. 38, p. 269, 1907.

[2]) Proceedings of the London Mathematical Society Ser. 2, Vol. 9, p. 434—448, 1911.

[3]) Proc. of the Lond. Math. Soc., l.c., p. 448.

[4]) For definitions of the mean-values of order p we refer to BROMWICH, op. cit., § 122, 123 and LANDAU, Darstellung und Begründung einiger neuerer Ergebnisse der Funktionentheorie, § 5.

[5]) Proceedings Vol. XXVI (p. 216—225).

$$\varphi_k(x) = \sum_1^\infty [A_n^{(k)} - A_{n-1}^{(k)}] \cdot x^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\varphi_0(x) = \sum_1^\infty a_n x^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

$$\varphi_k(x) + (1-x) \cdot \varphi_k'(x) = \varphi_{k-1}(x) \quad . \quad . \quad . \quad . \quad (2)$$

$$n \cdot [A_n^{(k)} - A_{n-1}^{(k)}] = A_n^{(k-1)} - A_{n-1}^{(k)} \quad . \quad . \quad . \quad . \quad (3)$$

With the aid of (2) we have proved [1]) that $\lim_{x \to 1} \sum_1^\infty a_n x^n = s$ implies

$$\lim_{x \to 1} \varphi_k(x) = s.$$

Now, if moreover:

$$| n \cdot [A_n^{(k)} - A_{n-1}^{(k)}] | < c,$$

we have by theorem 1 that $\sum_1^\infty [A_n^{(k)} - A_{n-1}^{(k)}]$ converges to s, i. e.:

$$\lim_{n=\infty} A_n^{(k)} = s$$

or: Σa_n is summable of order k.

Since

$$A_n^{(k)} = \frac{A_1^{(k-1)} + A_2^{(k-1)} + \ldots + A_n^{(k-1)}}{n}$$

we infer from $|A_i^{(k-1)}| < c$: $|A_i^{(k)}| < c$ and by (3):

$$| n [A_n^{(k)} - A_{n-1}^{(k)}] | < 2c.$$

Hence we see that:

$$| A_i^{(k-1)} | < c \text{ and } \lim_{x \to 1} \sum_1^\infty a_n x^n = s$$

imply that Σa_n is summable of order k.

We use in § 2 the particular case that $k = 1$. It then runs:

Theorem 3: *If* $\lim_{x \to 1} \sum_1^\infty a_n x^n = s$, *and* $|s_n| < c$, *then* $\lim_{n=\infty} \sigma_n = s$, *where*

$$\sigma_n = \frac{s_1 + s_2 + \ldots + s_n}{n}.$$

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[1]) Loc. cit. p. 222.

§ 2.

We now prove the following theorem:

Theorem 4. *If* $1 < k_1 \leq \frac{r_{n+1}}{r_n} \leq k_2$, and $k_1 > 1 + \frac{k_2^2-1}{2k_2}$, *then* $f(x) = x^{r_0} - x^{r_1} + x^{r_2} - \ldots$. *does not tend to a limit as* $x \to 1$ [1]).

Proof: We show that the series of coefficients of $f'(x)$ (which consists of the terms 1, $(r_1 - r_0 - 1)$ zeros, -1, $(r_2 - r_1 - 1)$ zeros, 1, and so on...) is *not* summable of the first order, i.e. that σ_n does not tend to a limit as $n \to \infty$. Then it is impossible that $f'(x)$ should tend to a limit as $x \to 1$, for this implies by theorem 3 the existence of $\lim_{n=\infty} \sigma_n$ [2]).

We show that σ_n does not tend to a limit if $n \to \infty$, by calculating two positive numbers γ and m so that:

$$\sigma_{r_{2p+1}} - \sigma_{r_{2p}} > \gamma \quad \text{if} \quad p > m.$$

We have:

$$\sigma_n = \frac{s_1 + s_2 + \ldots + s_n}{n} = \frac{n a_1 + (n-1) a_2 + \ldots + [n - (n-1)] a_n}{n}$$

$$\sigma_{r_{2p}} = \frac{r_{2p} - [r_{2p} - r_1 + 1] + [r_{2p} - r_2 + 1] - \ldots + [r_{2p} - r_{2p} + 1]}{r_{2p}}$$

$$= 1 + \frac{r_1 - r_2 + r_3 - \ldots - r_{2p}}{r_{2p}} = 1 - \frac{r_{2p} - r_{2p-1} + r_{2p-2} - \ldots - r_1}{r_{2p}}$$

Since $1 < k_1 \leq \frac{r_{\nu+1}}{r_\nu} \leq k_2$, it follows that $r_{\nu+1} \geq r_\nu k_1$ and $r_{\nu+1} - r_\nu \geq (k_1 - 1) r_\nu$. Substituting this in the expression for $\sigma_{r_{2p}}$ we have:

$$\sigma_{r_{2p}} \leq 1 - \frac{(k_1-1) r_{2p-1} + (k_1-1) r_{2p-3} + \ldots + (k_1-1) r_1}{r_{2p}}$$

$$\leq 1 - \frac{k_1 - 1}{k_2} \cdot \frac{r_{2p-1} + r_{2p-3} + \ldots + r_1}{r_{2p-1}}$$

$$\leq 1 - \frac{k_1 - 1}{k_2} \left[1 + \frac{1}{k_2^2} + \frac{1}{k_4^2} + \ldots + \frac{1}{k_2^{2p-2}} \right]$$

$$\leq 1 - \frac{k_1 - 1}{k_2} \cdot \frac{1 - \frac{1}{k_2^{2p}}}{1 - \frac{1}{k_2^2}}$$

[1]) We suppose $r_0 = 1$.

[2]) The condition $|s_n| < c$ is satisfied since s_n is 1 or 0.

$$\sigma_{r_{2p+1}} = \frac{r_{2p+1} - [r_{2p+1} - r_1 + 1] + [r_{2p+1} - r_2 + 1] - \ldots - [r_{2p+1} - (r_{2p+1} - 1)]}{r_{2p+1}}$$

$$= \frac{-1 + r_1 - r_2 + r_3 - \ldots + r_{2p+1}}{r_{2p+1}} = \frac{r_{2p+1} - r_{2p} + r_{2p-1} - \ldots + r_1 - 1}{r_{2p+1}}$$

$$\sigma_{r_{2p+1}} \geq \frac{(k_1 - 1)\, r_{2p} + (k_1 - 1)\, r_{2p-2} + \ldots + (k_1 - 1)\, r_2 + k_1 - 1}{r_{2p+1}}$$

$$\geq \frac{k_1 - 1}{k_2} \cdot \frac{r_{2p} + r_{2p-2} + \ldots + r_2 + 1}{r_{2p}}$$

$$\geq \frac{k_1 - 1}{k_2} \cdot \left[1 + \frac{1}{k_2^2} + \frac{1}{k_2^4} + \ldots + \frac{1}{k_2^{2p}}\right]$$

$$\geq \frac{k - 1}{k_2} \cdot \frac{1 - \frac{1}{k_2^{2p+2}}}{1 - \frac{1}{k_2^2}}$$

$$\sigma_{r_{2p+1}} - \sigma_{r_{2p}} \geq \frac{k_1 - 1}{k_2} \cdot \frac{1 - \frac{1}{k_2^{2p+2}}}{1 - \frac{1}{k_2^2}} - 1 + \frac{k - 1}{k_2} \cdot \frac{1 - \frac{1}{k_2^{2p}}}{1 - \frac{1}{k_2^2}}$$

$$\geq \frac{k_1 - 1}{k_2} \cdot \frac{2}{1 - \frac{1}{k_2^2}} - 1 - \frac{k_1 - 1}{k_2} \cdot \frac{1}{k_2^{2p}} \cdot \frac{1 + \frac{1}{k_2^2}}{1 - \frac{1}{k_2^2}}$$

Put $\dfrac{k_1 - 1}{k_2} \cdot \dfrac{2}{1 - \frac{1}{k_2^2}} - 1 = c$, then it follows from $k_1 > 1 + \dfrac{k_2^2 - 1}{2k_2}$ that $c > 0$. Hence we have:

$$\sigma_{r_{2p+1}} - \sigma_{r_{2p}} \geq c - \frac{\frac{c+1}{2} \cdot \left(1 + \frac{1}{k_2^2}\right)}{k_2^{2p}}.$$

Since $k_2 > 1$ the second term tends to zero as $p \to \infty$; hence it is possible to calculate whatever be γ between 0 and c an integer m so that:

$$\sigma_{r_{2p+1}} - \sigma_{r_{2p}} > \gamma > 0 \quad \text{if} \quad p > m.$$

Remark 1.

Of course it is sufficient that the relation $1 < k_1 \leq \frac{r_{n+1}}{r_n} \leq k_2$ is only satisfied provided $n >$ some finite number g, since the addition of a finite number of terms does not influence the existence or non-existence of a limit.

Thus the function $x - x^2 + x^3 - x^5 + x^8 - x^{13} + \ldots$ does not tend to a limit as $x \to 1$ since

$$1\frac{3}{5} \leq \frac{r_{n+1}}{r_n} \leq 1\frac{2}{3} \text{ if } n > 5 \text{ and } 1\frac{3}{5} > 1 + \frac{\left(1\frac{2}{3}\right)^2 - 1}{2 \cdot \left(1\frac{2}{3}\right)}.$$

Remark 2.

Strictly spoken we have proved theorem 2 only if the HÖLDER-mean-values are limited. Now the existence of a "Hölder-limit" of order k implies the existence of a "Cesaró-limit" of order k and vice-versa[1]); hence if we prove that the HÖLDER mean-values of order p are limited provided the CESARÓ mean-values of the same order are limited, then our theorem is proved for both classes of mean-values.

Now we have (see LANDAU l.c.):

$$H_n^{(k)} = T_2\, T_3 \ldots T_k\, (C_n^{(k)}) \quad \ldots \ldots \quad (1)$$

where $H_n^{(k)}$ is the n^{th} HÖLDER mean-value and $C_n^{(k)}$ is the n^{th} CESARÓ mean-value of order k, and:

$$T_p\,(x_n) = \frac{p-1}{p} \cdot \frac{x_1 + x_2 + \ldots + x_n}{n} + \frac{1}{p} \cdot x_n \quad \ldots \quad (2)$$

From (2) we deduce that $|x_i| < c$ implies $|T_k(x_i)| < c$; hence it follows from (1) that $|C_n^{(k)}| < c$ implies $|H_n^{(k)}| < c$.

[1]) Theorem of KNOPP-SCHNEE. See LANDAU, l.c.

Psychology. — "*On Subjective Rhythmisation.*" By F. F. HAZELHOFF and Miss HELEEN WIERSMA. (Communicated by Prof. E. D. WIERSMA).

(Communicated at the meeting of May 26, 1923).

Rhythmical perceptions, corresponding to rhythmical phenomena in the outer world, are at all times produced in numberless varieties by the rhythmical play of all sorts of physical and physiological processes. (Succession of day and night, of summer and winter, the heart-beat, the respiration, music etc.).

However, our perceptions are not always true reproductions of the reality round about us, as is borne out by many sensory illusions. The present authors are disposed to class among these illusions of perception also the peculiar phenomenon that we can perceive rhythmically a series of absolutely equal and regularly successive stimuli, which phenomenon has been termed "subjective Rhythmisation".

We purpose to discuss this phenomenon from a psychological view-point.

It was especially BOLTON (1) and MEUMANN (2) who pointed out the fact that regular series of auditory stimuli, i.e. auditory stimuli, precisely uniform quantitatively as well as qualitatively, and succeeding one another after equal intervals, can be perceived rhythmically, in any event when the rate of succession lies within certain bounds. KOFFKA (3) demonstrated the same with regard to visual stimuli, satisfying the same conditions.

This rhythmical perception of regular stimuli, however, is not restricted to visual-, and auditory sensations. The same rhythmisation also occurs in the department of touch. This we were able to demonstrate by a simple experiment.

Experiment: A regularly rotating axis is provided with a pointer that slightly touches the motionless hand of the observer at every revolution. The hand receives at every time precisely the same tick after precisely equal pauses (the rate of rotation may be regulated at will). The whole apparatus is hidden from the eye of the observer by a screen; neither can he see the pointer touching his hand.

By means of antiphones every auditory sensation is precluded so that the observer is entirely thrown back upon tactual sensations.

When we select a favourable rate of rotation, say 1 or 2 revolutions per second, subjective rhythmisation will soon reveal itself; at every time the observer will perceive with greater stress the 2nd or the 3rd touch, just as occurs with auditory-, and visual stimuli. It is also evident that with slow rates the observer will more readily apprehend a 2-rhythm; with increased rates, however, there is a greater aptitude for a 3-, or a 4-rhythm.

After some practice the observer will be enabled to work up to a different rhythm at every moment, either rising or falling. Suggestion imparted by his surroundings is of very great influence, but with a special rate of successive stimuli he generally selects a definite rhythm, most often a falling 2-rhythm (— ⏑), or a falling 3-rhythm (— ⏑ ⏑). However, other more complicated rhythms may occur.

Simple though this experiment may be, it is a great help to explain the nature of "subjective Rhythmisation", as it shows that this phenomenon is not restricted to auditory-, or visual sensations. It prompts us to assume that all sensory stimuli, which fulfil certain conditions, may be perceived rhythmically.

Let us first of all find an answer to the question what subjective rhythmisation really is. A periodic recurrence of "Betonungsunterschiede", "Innerliche zusammenfassung" (Meumann (2), and other much used terms are merely periphrastic designations of our experiences, they do not, however, explain their genesis. Neither is any explanation afforded by the mental pictures of rhythmic movements (such as dancing, the gallop of a horse and others), which in subjective rhythmisation are often aroused through association (Koffka (3)).

Introspection and the exact record of our experience, will have to show us the way here. We, therefore, made the following experiments; the observers were besides ourselves, 3 medical students.

Experiment: The observer is subjected to a regular series of auditory stimuli (we choose sound stimuli because sounds, indeed, are the better material for the perception of rhythm). The stimuli are applied in succession at a certain rate, about 1 to 2 stimuli per second, that quick or slow rate being selected with which the observer apprehends a certain rhythm most distinctly He is instructed to attend to what he hears, and to record accurately what he experiences by soft taps coinciding with every tick he hears upon a copper layer with a copper rod. As soon as the rod touches the layer an electric current, attracting an electromagnet, passes through. When the rod is raised again the current is broken, and the electromagnet returns to its original position. The electromagnet is provided with an inked pointer, which records the up-and-down movements on a rotating kymograph. In the curve thus obtained, the moment can be read at which the circuit is made (descending

movement of the pointer), as well as the time during which the current remains closed. The moment when the circuit is made is the moment when the observer imitates the tap, i. e. when he announces the moment at which he apprehends the sound stimulus; the time of the electric current represents the duration of auditory sensation. It is obvious that we can hardly expect absolute precision in this report, but important conclusions may be drawn from it with certainty, as already appears from the subjoined short portions of some curves.

The middle curve shows the reproduction of the auditory sensation of the observer, the upper one is an illustration of the stimulus itself. This stimulus consisted of a series of ticks given by an electrical hammer. The moment the regularly moving hammer touches the layer, thereby eliciting the sound-stimulus can readily be registered electrically in the same way as the taps given by the observer. The bottom curve shows the time in $^1/_{25}$ seconds:

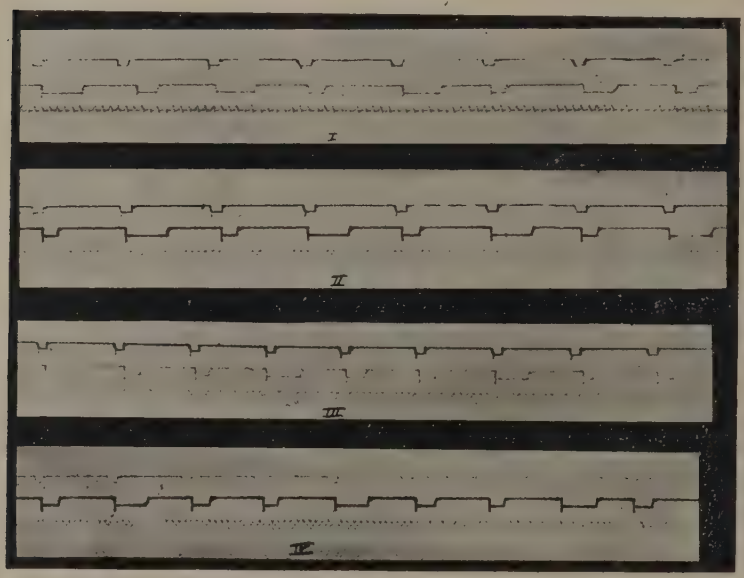

Fig. 1.

I. Falling 2-rhythm ´ ˘
II. Rising 2-rhythm ˘ ´
III. Falling 3-rhythm ´ ˘ ˘
IV. Amhybrachic 3-rhythm ˘ ´ ˘

We have measured the intervals of time between the records of the moments at which the observer announces the perception of the auditory stimulus.

The results of the measurements are given in the annexed tables:

I. Falling 2-rhythm (⏑ –).

Observer.	Number of measured 2-rhythm.	Time in 1/25 sec. between: beginning of non-accented and accented stimulus.	Time in 1/25 sec. between: beginning of accented and non-accented stimulus.	On an average the accented stimulus is perceived sooner than the non-accented in sec.:
B.	20	221	241	0,020
H.	20	249	264	0,015
Ho.	20	272	287	0,015
R.	25	284	292	0,007
W.	10	167	174	0,014

II. Rising 2-rhythm (– ⏑).

Observer.	Number of measured 2-rhythm.	Time in 1/25 sec. between: beginning of accented and non-accented stimulus.	Time in 1/25 sec. between: beginning of non-accented and accented stimulus.	On an average the accented stimulus is perceived sooner than the non-accented in sec.:
B.	25	330	315	0,012
Ho.	40	577	537	0,020
R.	40	470	444	0,013
W.	40	554	516	0,019

III. Falling 3-rhythm (⏑ ⏑ ⏑).

Observer.	Number of measured 3-rhythm.	Time in 1/25 sec. between: beginning 2nd non-accented and accented stimulus.	Time in 1/25 sec. between: beginning accented and 1st non-accented stimulus.	Time in 1/25 sec. between: beginning 1st and 2nd non-accented stimulus.	On an average the accented stimulus is perceived sooner than the: 1st non-accented in sec.:	On an average the accented stimulus is perceived sooner than the: 2nd non-accented in sec.:
B.	30	355	416	413	0,028	0,052
H.	10	141	168	145	0,068	0,044
Ho.	10	99	114	113	0,040	0,036
W.	20	267	272	271	0,004	0,006

IV. 3-rhythm. Amphibrachic (⏑ – ⏑).

Observer.	Number of measured 3-rhythm.	Time in 1/25 sec. between:			On an average the accented stimulus is perceived sooner than:	
		beginning 2nd non accented and 1st non-accented stimulus.	beginning 1st non-accented and accented stimulus.	beginning accented and 2nd non accented stimulus.	1st non accented in sec.:	2nd non accented in sec.:
B.	40	488	469	505	**0,017**	**0,018**
H.	30	372	348	390	**0,029**	**0,027**
W.	40	460	450	494	**0,018**	**0,026**

In all these cases, in which "subjective rhythmisation" readily manifested itself, and in which the observer reported his experience as accurately as could be, it is evident that

1°. the observer perceives the accented stimulus sooner than the non-accented

2°. that the perception aroused by the accented stimulus lasts longer, as is shown directly by readings from the curves, so that special measurements in this respect we considered superfluous.

That the observer perceives the accented stimulus with greater intensity is not expressed in the above curves, the deflection of the electromagnet being the same at every time. That this is a fact, however, is made manifest by introspection. As shown by the following curve this is also easily demonstrable by another method of recording, viz. by using a tambour instead of a copper layer for the accompanying taps of the observer. Owing to the slowness of the recording pointer these curves do not indicate small time-differences accurately; for this reason the measurements of time were taken from electrically registered curves only.

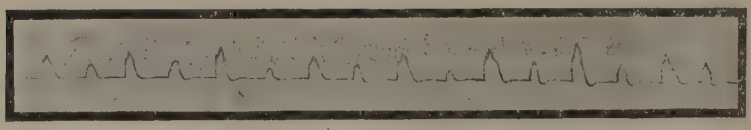

Fig. 2.
Falling 2-rhythm ⏑ – ⏑

In summary, then, the results of our curves illustrating the perceptions, lead to the following conclusions:

1. The subjective accented stimulus is perceived sooner.
2. It is perceived with greater intensity.
3. It is of longer duration.

Psychologically these three characteristics are easy to understand and may be explained upon the basis that a keener attention is given to one stimulus than to another, for we know that our perceptions are aroused sooner, that they become more intense, and that their after-effect lasts longer, according as our attention is more closely concentrated upon the stimulus.

This, in our judgment, is the nature of "subjective rhythmisation": *we attend more keenly to one stimulus than the other.*

Some points still require further elucidation. First of all the so-called "*Innerliche zusammenfassung*", the running-together of the impressions to form groups, which generally start with the subjective accented stimulus. This is also a temporal grouping, in such a sense that the elements of the group seem to follow each other at a quicker rate, while at every time there is a longer pause between two groups (MEUMANN (2)). We believe this grouping to be of a secondary nature and to result from the fact that the after-effect of the subjective accented stimulus is prolonged. This causes the pause between the termination of the accented stimulus and the beginning of the non-accented stimulus to be shorter than in the opposite case. This also accounts for the fact that rhythmisation always occurs in the sense of a falling rhythm, the shorter pause then falling within the group, or rather in consequence of the short pause it seems to us as if the stimuli by which it is bounded, belong together; conversely the long pause causes a separation between two groups. Another question that arises concerns the *cause of subjective rhythmisation*: why do we attend to one stimulus more keenly than to the other, and why is this alternation regular?

Our capacity of receiving outside impressions is limited. Of a large number of simultaneous stimuli to which we are exposed, we perceive only a part. Some attain a high state of consciousness, others are driven into the background of consciousness. When the stimuli are weak and affect us only for a short time, the quantity need not be large for a selection.

Experiment: two, three or more lines or points, perfectly equal *inter se*, are presented to the observer for a very brief period of time. When the lines or points are not very clear, and the exposure is short enough, only a few will be perceived well, the others appear to us much less distinct, or we do not see them at all.

In so short a period of time we cannot divide our attention among several weak stimuli so as to perceive all of them with the same distinctness. Now when such weak stimuli are presented in rapid succession, we may expect the same; also when they follow each other at short intervals, we cannot perceive all of them and we must make a selection. In our experimentation we also observed that it is exactly series of weak and obscure stimuli that are best adapted to subjective rhythmisation.

Now, *why* is this *accentuation regular?*

A periodically recurring stimulus is easy to perceive; we are beforehand predisposed to the impression, as we know when it is coming. When for instance of a series of stimuli we clearly apprehend the first and the third, we are better prepared for the fifth and the seventh. We may change this accommodation at will every moment so that we apprehend a 3- instead of a 2-rhythm, or we may substitute a rising for a falling rhythm.

The foregoing offers an explanation for other familiar features of subjective rhythmisation.

The quicker the rate of succesion of stimuli the larger will be the groups in which they are included. We endeavour to apprehend well as many stimuli as is possible, the slower the movement the larger will be the number of stimuli we perceive distinctly. When the rate of succession increases a 2-rhythm is changed into a 3-rhythm, a 3-rhythm becomes a 4-rhythm, etc.

It is also evident that the rate of the movement must not exceed certain bounds. When the pauses between two stimuli are too long, all our attention may be directed to every separate stimulus, the perception of every stimulus attains its maximal intensity, so that no rhythmisation will occur. When the pauses are too short, we cannot single out any stimulus, they run together into a vague entity.

It is also clear now that a *sensation of relaxation* (a pleasurable relief) is aroused when, after being constrained to intently follow a series of stimuli, we perceive them rhythmically, because of the much smaller demand upon our attention.

In experimenting it will be noted that the observer's aptitude for the rhythmic perception of a series of stimuli is ever increasing. Ultimately a certain rhythm will stick to him, it has so to say become an obsession.

It is just the same with special series of regular stimuli, which continually affect us in every-day life, such as the ticking of a clock, in which every one recognizes a rhythm, without being able to break away from it.

SUMMARY.

Rhythmical perception of a series of perfectly equal stimuli, following each other in regular succession, is aroused by the different degree of attention given to the various stimuli.

This divided attention is a necessary result of the fact that of a large quantity of stimuli operating upon us, only a limited number can be attended to (constriction of consciousness).

At the outset we can divide our attention at will, in the long run we may be constrained to do so.

The primary characteristics of subjective rhythmisation are based upon the fact that one stimulus is perceived after a shorter interval, with greater intensity and for a longer period of time than the other. The formation of groups results from it.

Subjective rhythmical perception can be aroused not only by visual-, and auditory-, but also by tactual impressions of stimuli that satisfy certain conditions.

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Physiology. — "*Researches on the chemical causes of normal and pathological Haemolysis*". By R. BRINKMAN and A. v. SZENT-GYÖRGYI. (Communicated by Prof. H. J. HAMBURGER),

(Communicated at the meetings of February 23 and April 26, 1923).

I. *Isolation of the haemolytic substances of normal human blood.*

It has been known for a long time that it is possible to isolate from normal blood by means of fat-extraction methods groups of substances, which possess strongly haemolytic properties. The study of these substances must be important for the explanation of normal and pathological haemolysis, but a definite result revealing their structure and manner of action has not yet been obtained. NOGUCHI [1]), when extracting these substances supposed them to be soaps, but he only examined them in regard to immunological phenomena and his views were not supported by later investigators [2]). Others were thinking of substances with a phosphatid structure, but could not give sufficiently conclusive proofs [3]).

A more exact investigation of the chemical constitution and the physico-chemical form, in which they exist in the blood, is wanted to be able to determine the physio-pathological significance of these substances. We have started from the idea, that it must be desirable to isolate these substances in a form as pure as possible, to be able to determine their chemical and physico-chemical properties. The first condition to be fulfilled was complete extraction of the haemolytic substances. Afterwards the extracts were fractioned under the guidance of their more and more increasing activity. This activity was tested by dispersing the extracts in isotonic neutral phosphate mixture at 37° [4]).

The determination of the haemolytics was carried out in the following way:

The human blood obtained by venapunction was defibrinated and sharply centrifugalized at once The corpuscles were imbibed in fat-free filterpapers and

[1]) NOGUCHI, Biochem. Zeitschr. VI. 327, (1907).

[2]) See LANDSTEINER. Handbuch KOLLE-WASSERMANN II, 1291, (1913).

[3]) BRINKMAN, l. c.

[4]) See for the method BRINKMAN Arch. néerl. de Physiol. VI, 451, (1922).

dried at 37°. Afterwards the red corpuscles were extracted for one hour by petrol-ether at room temperature; in this way neutral fat and most of cholesterin are extracted without any loss of haemolytics. The following quantitative extraction of haemolytics was made in a specially constructed small apparatus for "boiling-point extraction", with always freshly destilled fluid, adaptable for small quantities. As extraction-liquid acetone was chosen in analogy to the use of this liquid in phosphatid chemistry. In order to extract the haemolytics completely with acetone a preceeding treatment with alcohol-vapour for half an hour was necessary; the than following acetone-extraction dissolves all haemolytics in two hours.

To complete purification the acetone-extract was concentrated to a small volume and allowed to stand for one night in ice. In this way most of the dissolved substances are precipitated but no haemolytics are found in the precipitate. The remaining strongly active fraction has the following properties: it can be dissolved in all typical lipoid-dissolving liquids, if the reaction is slightly acid, but in an alkaline medium the haemolytics are insoluble is petrol-ether. The examined substances are not precipitated by cadmium, but they are precipitated quantitatively in aquous solution by barium and in acetone solution completely by an ammoniacal solution of acetate of lead, in the presence of not less than 30 % of water

So we see, that the investigated haemolytics show the typical reactions of the higher fatty acids. The said precipetate contained no phosphorus, so that phosphatides can be excluded definitely, *and the haemolytics, which can be extracted from normal blood must be identified with higher fatty acids resp. their soaps.*

The solubilty of the Pb and Ba salts indicated, that a mixture of fatty acids must be present, containing no or one and also more than one double linkage. Further experiments must determine the constitution and procentual concentration of these substances.

Separation of the fraction of the fatty acids and of phosphatids can only be obtained by careful quantitative methods of working; it is probable, that complete separation was not got by former investigators.

In addition to these results we have examined once more the haemolytic action of pure lecithin. If was found that a praeparation of lecithin purified by the newest methods showed no haemolytic properties; the haemolytic action of common trade lecithin must be ascribed to impurities, and this also is the case if this substance is somewhat purified by the usual acetone-precipitation.

With the knowledge, that the haemolytics of lipoid blood extract are higher fatty acids it is possible to isolate them in a simpler way. This may be done by the following method: the dried blood, sucked in filterpaper (5 cc. of blood) is treated with absolute alcohol for one hour in the boiling-point extraction apparatus. The extract

is concentrated to 5 cc. and than 5 cc. of a solution is added, which contains 0,2 n. Na_2CO_3 and 0,2 n. NaOH (in water). After five minutes the mixture is thoroughly shaken with 5 cc. of petrol ether; in this way neutral fats and cholesterin are eliminated completely and phosphatids for the greater part. The remaining alcoholic extract is acidulated with 0.5 cc. of HCl conc. and shaken with 2×5 cc. of petrol ether; afterwards 1 cc. of benzol is added to the alcoholic extract, and this is once more shaken with 5 cc. of petrol ether. The three petrol ether fractions thus obtained contain practically all normal haemolytics.

If this extract is dried and the residue emulgated in neutral isotonic phosphate mixture, then the amount of fatty acids obtained from 1 cc. of blood and emulgated in 1 cc. of phosphate solution may be diluted to $^1/_{64}$ and is still capable to haemolyse 1 % of blood corpuscles completely in half an hour at 37°.

CONCLUSION.

It is possible by means of lipoid extraction to isolate from normal blood substances wich are strongly haemolytic. These substances solely consist of higher fatty acids. A simple method is indicated for their quantitative extraction.

II. *The form in which strongly haemolytic fatty acids are contained in normal blood.*

In the previous communication it was stated, that a rather large quantity of intensively haemolytic higher fatty acids can be isolated from normal blood. It will be obvious that in normal blood this action must be completely on or nearly completely prevented; the mechanism of this inactivation is not definitely known. In this relation the formation of a protein-fatty acid compound was generally supposed, but we did not know if these combinations could exist in the blood plasma and if their haemolytic character has disappeared in this way. The knowledge of this inactivation must be important for the analysis of normal and pathological haemolysis, because insufficiency of the inactivation-mechanism must be dangerous to the corpuscles.

In order to investigate in which way the fatty acids are bound in the blood, we have made use of the high degree of capillary activity of these compounds; and this in the first place because this

surface activity is a property to which combining power and haemolytic action are intimately related, and secondly because the surface tension of small a amounts of blood can be measured accurately and easily by the torsion balance method [1]).

The surface-tension of a neutral highly diluted solution of fatty acids is much lower than the static surface tension of blood or serum. This fact already indicates that the fatty acids of blood cannot occur in the free state but must be bound somewhere. The minutest trace of free fatty acid must reveal itself immediately by a marked decrease of static surface tension, but the capillary-activity of the protein-fatty acid compounds also is, as far as we know, so intensive, the a decrease of surface tension plasma-air should be observed if an added fatty acid was bound as protein-compound.

The possible combination of protein and fatty acids may supposed to be primarely chemical or adsorptive; the last form would be probable by the intensive surface activity of these substances.

In the following table it is shown how the surface tension serum-air changes when small quantities of a diluted neutral emulsion of fatty acids are added.

Surface tension of fresh human serum.	52	Dyne c.M.
+ 0.001 N oleic acid in neutral emulsion.	52	„
+ 0.002 N „ „ „ „	52	„
+ 0.003 N „ „ „ „	52	„
+ 0.004 N „ „ „ „	51	„
+ 0.005 N „ „ „ „	47	„
+ 0.006 N „ „ „ „	45	„
+ 0.007 N „ „ „ „	42	„
+ 0.008 N „ „ „ „	41	„
+ 0.009 N „ „ „ „	39	„
+ 0.010 N „ „ „ „	39	„

It is seen, that 0,004 N. oleic acid may be added to serum without change of surface tension; when more acid is given, a gradual decrease of surface tension takes place till the value of ± 40 dynes/cm. has been reached. A further lowering is only to be seen, if large amounts of fatty acid are added. We will not delay upon the explanation of the gradual decrease of tension, but try to investigate the mechanism by which the plasma can preserve its original tension. Any marked lowering of this tension must be considered abnormal.

The constancy of surface tension indicates that the researched

[1]) Brinkman and Van Dam. Münch. med Woch. 1550 (1921).

fatty acid compound can not lower the surface tension of water to less that 52 dynes/cm. By this observation the hypothesis of inactivation of fatty acids by protein solely is proved to be insufficient. Therefore we had to think of other possible compounds und found a sufficient explanation for constancy in the formation of calcium soaps. The existence of this proces of inactivation was found in the following way:

A. If the Calcium of serum or blood is precipitated by addition of oxalate of ammonia, the surface tension can not be held constant if small quantities of oleic acid are added. This is to be seen in the next table.

Surface tension of fresh human oxalate plasma	49 d. c.M.
+ 0.001 N oleicacid in neutral emulsion	47 „
+ 0.002 N „ „ „ „	45 „
+ 0.003 N „ „ „ „	42 „
+ 0.004 N „ „ „ „	40 „
+ 0.005 N „ „ „ „	38 „

The same results are obtained, when NaFl plasma is used.

B. A salt-solution containing the same amount of Ca as Plasma can maintain its tênsion above 50 dynes on addition of a neutral emulsion of oleic acid at 37°, to the same extent as plasma can. This holds for a solution of $CaCl_2.6$ Aq. 0,05 % as well as for a solution composed of NaCl 0,7 %, $NaHCO_3$ 0,2 % KCl 0,02 %, $CaCl_2.6$ aq. 0.05 % and H_2CO_3 till $[H^{\cdot}] = 0{,}4.10^{-7}$ is reached.

The following table gives the surface tension of the said salt solution if small amounts of oleic acid were added very gradually.

Surface tension of the balanced salt-solution	74 d. c.M.
+ 0.0001 N oleicacid in neutral emulsion.	54 „
+ 10 × 0.0001 N „ „ „ „	53 „
+ 10 × 0.0001 N „ „ „ „	52 „
+ 10 × 0.0001 N „ „ „ „	52 „
+ 5 × 0.0001 N „ „ „ „	50 „
+ 5 × 0.0001 N „ „ „ „	39 „

If the surface tension of the saline shall not be lowered unter the plasma tension, it is necessary to add the oleic acid very gradually, and to leave the mixture for a half hour at 37° after each addition; only in this way it is possible to obtain a form of Oleate of Ca, whose capillary activity is low enough. But this condition is fulfilled in vivo.

The question now arose, wether this mechanism of inactivation would be equally important for the normal fatty acids of the blood as it proved to be for oleic acid. It is certain, that about one third part of the blood-calcium is present in the colloidal state; when we

consider the insolubility of Ca soaps it is possible, that the indiffusible part of the plasma Ca will consist wholly or partially of soaps. It is easily to be shown, that complete precipitation of the blood Ca is followed by a marked decrease of surface tension.

Surface tension of one cc. of freshly taken human serum is 53 dynes/cm; when 0,3 ccm. of a saturated solution of oxalate of ammonium is added, it decreases to 50, 48, 46 dynes/cm. The action of NaFl is similar.

Further if at little acid is added to the plasma, the fatty acids must be liberated from the eventually existing Ca soap compound. This proved to be the case; the amount of HCl necessary to lower the surface tension of serum from 52 to 45 dynes is exactly equivalent to the potential alkalinity of that serum. So it is probable that in normal blood also a great deal of the fatty acids are circulating in the form of Ca compounds. Direct chemical analysis will have to bring further evidence.

Till now we only examined the inactivation of oleic acid; the saturated fatty acids appear to be bound in the same way, but the physiologically important highly unsaturated linolenic acid give Ca salts, which lower the surface tension of the balanced salt solution to 38 Dynes. In accordance with this the blood or plasma it is not capable to maintain its surface tension if a small amount of isotonic neutral emulsion of linolenic acid is added, contrary to what occurs when oleic acid is given. This is seen from the following experiment.

Surface tension of fresh human serum	53 dynes p. cm.
+ 0.001 N linolenic acid emulsion	47 „ „
+ 0.002 N „ „ „	46 „ „
+ 0.003 N „ „ „	46 „ „
+ 0.004 N „ „ „	44 „ „
+ 0.005 N „ „ „	43 „ „

Although linolenic acid also is in plasma subject to considerable capillary inactivation, this process is not so complete, that the surface tension can be maintained absolutely constant. This fact must be explained by the capillary activity and solubility of the linolenate of Ca.

By these circumstances the higher unsaturated fatty acids circulating in the blood must have a great biological importance, because their Ca inactivation is failing. Therefore these acids must be bound by plasma colloids or corpuscles with decrease of interfacial tension. If now the inactivation of fatty acids extracted from corpuscles is compared in serum and in salt solution with the process described, it appears that these substances have the same properties as saturated

acids, and oleic acid have, but that a very small fraction is present which acts in the plasma as would do linolenic acid. Addition of fatty acids extracted from blood lowers the surface tension of serum from 53 dynes to 49,5 dynes; when more extract is added, the tension remains as constant as if oleic acid were added. The extracted fatty acids lower the surface tension of the serum to that of total blood, for corpuscles also can decrease the surface tension of serum to 50 dynes. So the tension of *blood* is not decreased by extracted fatty acids. If it may be concluded, that a small fraction of highly unsaturated fatty accids is absorbed normally to the corpuscles, this must be verified by further investigation.

In a following communication we will describe the influence which the investigated mechanisms of inactivation have on normal and pathological haemolysis.

SUMMARY.

By means of determination of surface tension of blood and serum it was shown, that the normal fatty acids of the blood or also those added on purpose are bound in the form of Calcium soaps, by which mechanism their capillary activity is decreased considerably. It is very probable, that this formation of a Calcium compound is the cause of disappearance of haemolytic properties of stearic acid, palmitinic acid and oleic acid in serum. The inactivation by means of Ca is not present in the case of linolenic acid; by this circumstance the haemolytic character of this substance of serum will be much greater.

III. *Experimental anaemia caused by injections of linolenic acid.*

In a previous communication it was pointed out, that higher fatty acids in the blood generally are circulating as Ca compounds, and thus have lost their marked capillary activity. It was stated however, that the Ca soaps of the higher unsaturated fatty acids i.e. of linolenic acid, do not loose their capillary activity, and that by this reason we have to expect much greater haemolytic action in vivo of this substance.

It was shown, that linolenic acid is an intravital haemolytic substance, of great activity and that there is no direct inhibition of the action of linolenic acid in the plasma. It was known for a long time, that injection of the saturated fatty acid or of oleic acid can not cause a distinct intravital haemolysis, probably by the mechanism of Ca inactivation, described formerly. In the case of linolenic acid

the injection is followed by marked haemolytic symptoms, as appeared from the following experiments.

Intravenous injection. A rabbit of 3620 gr. is injected in the auricular vein 0.250 gr. of linolenic acid dispersed in 10 ccm. of isotonic phosphate mixture. After 10 minutes the surface tension of the blood, which otherwise is 54,5—55,5 dynes/cm is decreased to 50 dynes and the serum is coloured lightly reddish. If now the surface tension is measured with regular intervals, it is seen, that the surface tension can not rise to the normal value but always has a value of 50 dynes approximately. The haemoglobinaemia is increasing more and more. After twenty minutes a strong haemoglobinuria is observed, and the rabbit makes a very sick impression. One hour after injection the animal dies with symptoms of utmost anaemia and dyspnoe.

In this way we could prove by several experiments, that a rabbit is killed by intravenous injection of ± 100 mg. of linolenic acid per Kg. under symptoms of very strong haemolysis. If smaller quantities of linolenic acid are given intravenously, the rabbit is not killed at once, but a chronic haemolysis with severe anaemia, urobilinuria, etc. sets on. When the linolenic acid is given intravenously, there is always a certain chance, that a little too large dosis of linolenic acid will lead to a direct mortal haemolysis.

A severe chronic haemolytic anaemia is produced by the subcutaneous, or better intramuscular injection of the acid. In this case the greater part of the injected substance seems to be inactivated and the following discase develops itself.

A rabbit of 3450 gr. in good state of health. Number of red cells 5,400,000. Haemoglobin 60 (Sahli). The form of the red cells in plasma is purely biconcave; a very small degree of anisocytosis, no polychromatophilia, absence of normoblasts. The serum is colourless and does not contain bilirubin. No uroblin or urobilinogen in the urin. The surface tension of the blood is 55,4 dynes at 19°.

The rabbit is injected every day with 200 mgr. of linolenic acid intramuscularly. After the first injection the surface tension of the blood decreases to 51—52 dynes, and remains so during all the experiment. 2—3 days after beginning of the treatment an intensive urobilinuria sets on and does not disappear during the course of injections. The blood picture shows from the third day a more and more increasing anisocytosis and polychromatophilia, while the number of irregularly shaped cells and sphaeric cells is rising. After five days the number of red corpuscles was lowered to 2.500.000; after that the first regeneration showed itself with numerous normo-

blasts, and strong anisocytosis and polychromatophilia. The number of red cells at this time was 3.700.000, the haemoglobincontent 55. So the index had increased distinctly and this increase remains very marked during the course of injections.

Twelve days after the first injection the number of red cells had decreased again till 2.900.000 (Haemoglobin (45), and the second period of regeneration began. Now the blood picture demonstrated the typical symptoms as they are found in distinct pernicious anaemia. Especially macrocytosis, poikilocytosis, strongly disshaped corpuscles, polychromatophilic megalocyts and normoblasts were striking. Bilirubinaemia could only be traced in the rabbit in cases of strong acute haemolyses. In the more chronic forms this phenomenon is not observed, urobilinuria being very marked however.

The rabbit is emaciated and makes a sick impression. If the injections are stopped in the beginning, the anaemia may be cured; if the treatment is continued, the typical pernicious symptoms will last.

So there is no doubt, that intramuscular injection of linolenic acid causes a chronic haemolytic anaemia in a short time, the red picture of which is showing all typical marks of pernicious anaemia. The picture of white cells has not yet been researched till now. We shall have to make a more exact analysis of this anaemia by linolenic acid, but it may be stated already, that linolenic acid is a very severe haemolytic substance. As it was found in the previous communications, we must ascribe this intravital action to the fact, that the Ca soaps of higher unsaturated fatty acids are capillary active and haemolytic, contrary to the Ca soaps of palmitinic acid and oleic acid.

Now this acid, forming an important percentage of the phosphatid fatty acids, it is practically certain, that the formerly used praeparation of trade-lecithin could effect the described haemolytic action by the rather large content of linolenic acid. Linolenic acid is a substance, which is found in the biochemistry of fat and phosphatid metabolism and it is probable, that this acid is circulating in normal blood.

In fact we were able to demonstrate by means of specific extraction, that in the 0,6—0,7 mgr. of fatty acids, which are found in one ccm. of normal human blood there is always present a small fraction consisting of higher unsatured fatty acids.

It appeared further, that all other fatty acids of the blood are inactivated by serum, in regard to capillary active and haemolytic action, but this small fraction of higher unsaturated fatty acids can

not be inactivated completely, so that we must ascribe a great importance as a physiologically haemolytic substance to the normal circulating linolenic acid. We will try, to determine the concentration of linolenic acids in the severe human anaemias.

SUMMARY.

Intramuscular injection of 200 mg. of linolenic acid per day in the rabbit is followed in a short time by chronic haemolytic anaemia. The blood picture shows a striking resemblance to that in pernicious anaemia.

Intravenous injection of ± 100 mgr. of linolinic acid pro Kg. causes a letal haemolysis.

Chemistry. — "*Nitrogen fixation by means of the cyanide-process and atomic structure.*" By Dr. L. HAMBURGER. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of June 30, 1923).

a. *Introduction.* It is known that the reaction

$$MCO_3 + 4\,C + N_2 = M(CN)_2 + 3\,CO$$

forms the foundation for the nitrogen fixation by the so called cyanide process. For this conversion the temperature at which the capture of the nitrogen takes place with practically appreciable velocity appears to be very divergent, according as another M is chosen for the metal. H. LUNDÉN [1]) has also included rubidium and ceasium in his researches, and is of opinion that there is a relation between the boiling-points and atomic weights of the metals in question and the "cyanizing-temperature". It is, however, not possible to derive a quantitative relation on this foundation.

b. *Stages of the cyanizingreaction.* In order to arrive at a clear insight the fact should be considered that according to J. E. BUCHER [2]), two stages before all should be distinguished in the course of the reaction:

$$\text{I.}\quad MCO_3 + 2\,C = M + 3\,CO$$
$$\text{II.}\quad M + 2\,C + N_2 = M(CN)_2.$$

Of these reactions I bears an exceedingly endothermal character, II on the other hand, is strongly exothermal, II takes place practically momentarily (either with addition of a catalyst or without). Whether a practically appreciable reaction-velocity will appear, will therefore depend on I. The strongly endothermal character of I [3]), however, causes the temperature to remain pretty well constant, when the reaction sets in, till the reaction of MCO_3 has been completed. The quantities of energy required for this are so great, that, especially at comparable conditions, factors like energy-quantities,

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[1]) Cf. TH. THORSELL. Zeitschr. f. angew. Chem. **33**, 251 (1920).

[2]) J. E. BUCHER. Jl. of Ind. and Eng. Chem. **9**, 233 (1917).

[3]) In consequence of which the total reaction I + II is also still endothermal in a high degree.

required for division, dilution, solution, melting and evaporation remain of subordinate importance [1]). Hence notwithstanding the complicated character, we have to do with:

1. comparatively characteristic reaction temperatures;
2. with the decisive influence of metal-formations.

We can now divide I again into the following more elementary processes:

$$a.\ MCO_3 = MO + CO_2 \qquad c.\ O + C = CO$$
$$b.\ MO = M + O \qquad d.\ C + CO_2 = 2\,CO$$

in which c and d follow the same reaction equation for all metal cyanide-syntheses, whereas b is first of all the reaction which claims the lion's share of the energy-supply.

c. *The primary reaction.* From W. KOSSEL's [2]) point of view the course of b means only this, that under the influence of the supplied energy in the metal oxide the oxygen cedes again the negative electron taken from the metal. In our case this view entails the difficulty that this restitution would have to take place more easily with metal atoms with relatively great affinity to the returning electron than to more electro-positive elements. In reality, however, the reaction appears to set in more easily with increasing electro-positivity of the elements.

It is, however, not necessary to assume that in every metal-metalloid compound one or more of the metal-electrons has quite gone over to the metalloid. In many cases it may be more a question of partial transition, i. e. conditions will be found in which only partial separation ("Lockerung", dislocation) of the metal- (valency-) electron with regard to the metal atom must be assumed. In connection with the spectral interpretations by BOHR this may also be expressed thus, that the electron in question will on an average be at the disposal both of the oxygen atom and of the metal atom in a characteristic "abnormal" path.

The decreasing reaction temperature with the increasing electro-positivity of the metal leads us further to the assumption that pri-

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[1]) In the same way the dependence of the reaction-energy on the temperature may be neglected within a wide margin. The possibility of all these approximations stamps the cyanizing-reaction as one of the few chemical conversions, which like the rare ideal photo-chemical reactions are able to give experimentally demonstrable indications in favour of the theories which at the same time bear a fundamental and idealizing character [cf. e. g. F. WEIGERT, Zeitschr. f. Phys. **14**, 383 (1923)].

[2]) W, KOSSEL, Ann, d. Phys. **49**, 229 (1919).

marily the electron does not entirely return to the metal atom, but that inversely a complete separation of the valency-electron from the metal rest should be taken into account. It is this process that we shall subject to a fuller examination in what follows, and which we shall briefly denote by the expression of "primary reaction". [1])

Hence we come to realize the possibility of the conclusion that the dissociation of the metal oxide does not take place by the direct process of splitting up $MO = M + O$, but that with increase of energy first an *activation* sets in, manifesting itself as formation of ions. From this activated condition the further course of the reaction takes place.

Thus we are led to place ourselves on the basis of these theories of reaction-velocities which have appeared to possess remarkable validity, at least in definite cases; particularly we come to the "activation" basis given as of general validity first by Sv. ARRHENIUS [2]) and later among others by J. PERRIN [3]) in his "Lumière et Matière".

d. Ionisation Potential.

It is known that the ionisation potential of the vapour is a decisive quantity for the detaching of an electron from a free metal atom. Where there is reason to assume that the primary reaction takes place in the gasphase [4]) we will first of all try, in connection with the view about the primary reaction given under *c*, in how far the ionisation potential can also govern the cyanizing-reaction. For this purpose we will calculate the values of the quantity $\frac{V}{T}$ according to the table below, in which V represents the ionisation potential

[1]) A possible addition of the separated electron to the oxygen rest should be considered as a second stage. From J. FRANCK's researches on the collisions of slow electrons in electro-positive and noble gases we know that negative electrons are seized by oxygen, but are on the contrary under certain conditions relinquished by the electro-positive atom. In the same way a partially bound electron, which gets free through "critical" energy supply with small velocity [thus the lower limit of energy supply required to bring about the primary reaction may be indicated for brevity], may be bound to the oxygen atom. We leave this out of account in the next close examination of the primary reaction.

[2]) Sv. ARRHENIUS. Zeitschr. f. Phys. Chem. **4**, 226 (1889).

[3]) J. PERRIN. Ann. d. Phys. **11**. 5 (1919).

[4]) All the metal carbonates or oxides of the alkalies and earth-alkalies are greatly or appreciably volatile at the indicated reaction temperatures. In the dissociable carbonates the evaporation is promoted by the formation of oxydes in molecular distribution (formation "in statu nascendi" and transportation by the gas current). The parallelism between the cyanizing temperature and volatility of the carbonates resp. oxydes is striking.

of the free alkali-resp. earth alkali atoms, and T the cyanizing-reaction-temperature.[1]) It is seen from the fourth row of the table that the same order of magnitude is found everywhere for $\frac{V}{T}$.

Row 1	Metal	Li.	Na.	K.	Rb.	Ce.	Mg.	Ba.	Sr.	Ba.
2	Reaction-temp. in °K(T)	1370	1200	1100	970	870	2100?	1900	1670	1320
3	Ionisation-potent. in volts (V)	5.4	5.1	4.3	4.2	3.9	7.6	6.1	5.7	5.2
4	$\frac{V}{T}$. 10^3	4.2	4.2	4.0	4.2	4.3	3.2?	3.2	3.4	3.9
5	Excitation potential V'' in Volts	1.84	2.09	1.60	1.55	1.38	2.70	1.88	1.79	1.56
6	$\frac{V - V''}{T}$. 10^3	2.5+	2.5	2.5—	2.7	2.86	2.3	2.2	2.3	2.7

Considering the widely divergent circumstances the agreement may even be called remarkable, the more so as a perfectly sharply defined reaction temperature cannot be expected on theoretical ground either.

e. Dislocation potential.

The ionisation potential determines the energy required to detach an "outer" electron of a metal atom entirely from a normal path. As under *c* we arrived at the view that in the compound the electron in question is present in an abnormal path, the conclusion is obvious that not V, but a smaller quantity $V - V'$ can give a measure for the critical supply of energy, in which V' is a quantity which determines the difference of energy between the electron in the abnormal path of the compound and the electron in the free metal atom, that is in the normal path. We shall call this quantity briefly dislocation potential, the electron in the abnormal path will be called dislocated electron.

The separation of the dislocated electron from the metal rest must, in our opinion, require a quantity of energy that is proportional to

[1]) The value of the reaction temperature of CaO is taken from a communication by P. Schläpfer (Schweiz. Chem. 1919, Heft 29 (30), the values of the ionisation-potential are derived from a summary given bij J. Franck (Phys. Zeitschr. 22, 413 ('21). The values of T taken for *Mg* and *Ca* will be discussed elsewhere, among others because reduction- and cyanizing-temperature (resp. the temp. of the formation of metal cyanamid) differ considerably for (the compounds of) these elements.

$e\,(V-V')$ (in which e represents the charge of the electron), and which is derived from the available thermal energy of the medium. Putting the latter in approximation proportional to T, we find:

$$e\,(V-V') = kT,$$

so that the following relation is found:

$\frac{V-V'}{T}$ must be constant for all cyanizing reactions.

f. Excitation potential.

With the analogous structure of the "outer electron shells" of the homologous elements it is probable that in the metal oxide the dislocated electron as a rule and on an average will be in a corresponding abnormal path. With the available date we can, however, not say which. When we, however, compare the values of the excitation tension V'' of the different elements, which quantity is decisive for the energy-supply required to transfer an "outer" electron in the metal atom from the normal into the first abnormal path (Row 5 of the table) with the ionisation potential (row 3), the analogous course of these values with increasing electro-positivity of the elements, is striking. When we, therefore, introduce the quantity V—V'' instead of V—V' we should, reasoning in the same line, obtain practicable results not only for these cases in which the abnormal path of the valency electron in the compound would be identical with the first abnormal path, but also when the position of the dislocated electron would be identical with another abnormal path. A considerable difference between V'' and V' is, however, unlikely, because then the value of the quantity V—V'' would no longer be in accordance with the considerable energy-supply required if the primary reaction is to take place [1]).

In row 6 the values are recorded of the quantity $\frac{V-V''}{T}.10^3$. It is seen that the difference between the alkalies and the earth alkalies is smaller than in row 4. Considerations for a further correction wil be given elsewhere.

g. In conclusion we will remark that with the aid of RUTHERFORD-BOHR's atomic model we have endeavoured in the above to

[1]) This is the more cogent as moreover at the complete addition of the "outer" electron to the oxygen rest energy is liberated. We have not considered this more closely, because this increase of energy with regard to the oxygen rest may be put equal for all the metal oxydes considerated, and can therefore not give occasion to characteristic differences. [See also "note at the correction"].

give an example of the view that at least in definite cases, ionisation- and dislocation-potentials are not only decisive with regard to the possibility of reaction, but also with regard to reaction velocity and reaction temperature.

PERRIN sees photo-chemical action in every chemical action. Our insight into the structure of the atom makes us realize that the fundamental feature is the displacement of the electrons in it. This displacement may be brought about by radiation, but also in various other ways. Accordingly it is not justifiable to assign merely a part to light in the explanation of chemical action; other forms of energy also make their influence felt. In connection with the conception of an interaction between the different forms of energy, the possibility might, however be considered of a derivation, even though it be a formal one, of the relation $\frac{\text{critical energy supply}}{\text{reaction temperare}} =$ constant from the laws of radiation, in which case the directing lines given by R. C. TOLMAN [1]) and E. K. RIDEAL [2]) should be taken into account. This will be treated elsewhere.

Dordrecht, June 26th 1923.

Note at the correction. From recent determinations of the electron-affinity of some electronegative elements as well as from known electro-chemical date may be deduced — as will be shown elsewhere — that the addition potential of an electron to an atom of oxygen can at most be about 2 volt. This value confirms the assumptions given sub *f* and justifies the neglect of the addition potential of the valency-electron to the oxygen, the value of which in our cases (as a rule) can only be little.

July, 4th, '23.

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[1]) R. C. TOLMAN. Journ. Amer. Chem. Soc. **42**, 2506 (1921).

[2]) E. K. RIDEAL. Phil. Mag. **42**, 156 (1921).

Bactériologie. — *„Culture du bactériophage sans intervention de bactéries vivantes"*, par F. d'Herelle.

(Présenté par Mr. le Prof. W. Einthoven dans la séance du 26 mai 1923).

On sait que l'activité des différentes souches du Bactériophage est essentiellement variable, cette activité se mesure par l'intensité de l'action destructrive vis-à-vis des bactéries sensibles. Un Bactériophage au maximum d'activité, introduit a l'unité dans une émulsion bactérienne, provoque la dissolution totale des bactéries présentes; le milieu est, l'action terminée, aussi limpide que du bouillon filtré et reste tel indéfiniment. Ces souches au maximum d'activité sont rares dans la Nature, c'est pourtant exclusivement a de telles souches qu'il faut s'addresser pour étudier et comprendre le mécanisme intime du phénomène de bactèriophagie qui, avec des souches moins actives, est déformé ou masqué par des phénomènes secondaires liés à la résistance des bactéries.

En possession d'une souche du Bactériophage possédant une activité maxima vis-à-vis d'un Staphylocoque blanc, j'ai tenté la culture de ce Bactériophage aux dèpens d'une émulsion de la bactérie sensible, non plus vivante comme dans toutes les expériences jusqu'ici realisées, mais morte.

Le Staphylocoque sensible est cultivé sur bouillon gélosé; après 24 heures d'incubation la surface de la gélose est lavée avec une petite quantité d'eau salée à 9 p. 1000: on obtient une émulsion épaisse qui, répartie dans des tubes qui sont scellés, est maintenue pendant une heure dans un bain-marie règlé à 58—60° C. La sterilité est vérifiée par ensemencements.

Cette émulsion épaisse est répartie dans des tubes renfermant 10 c.c. d'eau distillée sterilisée, salée à 9p. 1000, de manière a obtenir une opacité correspondant environ à 200 millions de Staphylocoques tués par c. c. Tel est le milieu employé pour la culture du Bactériophage.

Un tube de ce milieu est ensemencé avec 10^{-2} c.c. d'une émulsion en bouillon du Staphylocoque vivant, dissoute sous l'action du Bactériophage en expérience puis filtrée. Le tube est placé à l'étuve à 37° pendant 24 heures. 10^{-2} c.c. de la première èmulsion est alors introduit dans un second tube, renfermant 10 c. c. de l'émulsion

du Staphylocoque tué par la chaleur. Les passages successifs étan ensuite continués de même manière.

Au dixième passage, le taux, facilement calculable, de la dilution du centième de c. c. du liquide renfermant le Bactériophage, introduit dans le premier tube de la série, est de 10^{-30}. Si le Bactériophage se trouve encore dans ce dixième tube, on peut être certain qu'il y a eu culture car, du liquide introduit dans le premier tube, il ne pourrait rester dans ce dixième tube qu'une fraction d'un électron, par suite des dilutions successives. D'autre part on ne peut admettre que le Bacteriophage soit constitué par des corpuscules ne représentant qu'une fraction d'un électron.

Or, après incubation, 13^{-7} c. c. de l'émulsion du dizième passage, introduit dans uns émulsion en bouillon du Staphylocoque vivant provoque une bactériolyse totale: preuve que le Bactériophage s'est maintenue à travers les passages. Il n'a donc pu se multiplier qu'aux dépens des bactéries mortes.

Je suis arrivé actuellement au vingt-troisième passage (dilution du liquide primitif 10^{-69}): après 24 heures d'incubation l'activité de l'émulsion est la même qu'au dizième passage. c'est à dire que 10^{-7} c. c. introduit dans une émulsion en bouillon de la bacterie vivants provoque la bactériolyse.

Je me suis naturellement assuré que l'émulsion seule du Staphylocoque tué par la chaleur, de même d'ailleurs que vivant, ne possède aucune propriété bactériolytique.

Le Bactériophage se cultive donc indubitablement aux dépens de bactéries mortes. Contrairement à ce qui se produit lorsqu'il se cultive aux dépens de bactéries vivantes, les bactéries mortes ne sont pas dissoutes.

Les caractères du Bactériophage qui s'est développé dans une émulsion de bacteries mortes sont fort différents de ceux qu'il présente quand il se développe aux dépens de bactéries vivantes: dans ce dernier cas le Bactériophage présente une résistance à l'action de la chaleur et des antiseptiques, analogue à celle des spores bactériennes; cultivé aux dépens de bactéries mortes il est au contraire très sensible: il est tué par une exposition de quinze minutes à une température de 56° C. de même que par un séjour de dix heures dans l'eau renfermant 20 p. 100 d'alcool ou d'acétone; il ne résiste pas plus longtemps dans l'eau saturée d'éther ou renferment des traces d'iode. De plus il ne traverse plus les bougies de porcelaine, non pas a cause de ses dimentions (l'examen de préparation colorée ne montre ancun corpuscule visible), mais, vraisemblablement, porcequ'il est adsorbé par le filtre, ce qui se produit d'ailleurs pour

d'autres ultravirus. Par contre, la virulence ne semble pas atteinte car, mis en présence de bactéries vivantes, il provoque leur dissolution d'une maniére très active: il récupère alors ses propriétés de résistance à la chaleur et aux antiseptiques et il traverse les bougies de porcelaine, même serrées.

Ces différences de résistance confirment ce que des expériences antérieures semblaient déja indiquer; le Bactériophage présente deux formes: une forme végétative et une forme de résistance. Toutes deux coexistent dans les cultures aux dépens de la bactérie vivante: les formes de résistance ne pouvant vraisemblablement se produire que *dans* les bactéries vivantes. Dans les cultures en présence de bactéries mortes, seules existent les formes végétatives qui, des lors, se reproduisent uniquement par scissiparité.

J'ai effectué des expériences complementaires qui montrent que la culture du Bactériophage peut également s'effectuer dans des macérations du Staphylocoque tué *centrifugées*, c'est à dire dans un liquide de macération débarassé des corps microbiens: la forme végétative se cultive donc, non pas dans la bactérie tuée, mais dans le milieu, aux dépens des produits bactériens solubles.

Par des expériences antérieures, j'ai montré que le Bactériophage est un être autonôme, possédant des caractéres propres, indépendants de la bactérie qui subit son action, se qui donnait la preuve, qu'il se multiplie en milieu hétérogène. Ce fait implique le pouvoir d'assimilation chimique, caractère fondamental qui suffit pour caractériser la nature vivante de l'être qui le possède. Les présentes expériences ne font que confirmer la nature vivante du Bactériophage.

Nombre d'auteurs ont voulu expliquer le phénomène de bactériophagie et la reproduction du principe actif en cours d'action, comme un phénomène lié au métabolisme microbien. Cette explication, déjà contredite par le fait de l'autonomie du Bacteriophage, tombe définitivement devant le fait de la culture dans de l'eau salée ne renfermant que des bactéries mortes, ou même leurs seuls produits solubles, car une bactérie morte, ou ses produits solubles, ne sont plus qu'un assemblage de substances chimiques inertes, incapables d'aucun acte de métabolisme [1]).

(*Institut d'Hygiène tropicale de l'Université de Leyde*).

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[1]) Je tiens naturellement à la disposition des expérimentateurs la souche du Bactériophage avec laquelle j'ai realisé ces expériences.

Géologie. — *„Description de Crustacés décapodes nouveaux des terrains tertiaires de Borneo"*, par V. VAN STRAELEN.

(Présenté par Mr. le Prof. H. A. BROUWER dans la séance du 26 mai 1923).

Les Crustacés décapodes décrits dans cette note, ont été recueillis par M. le Dr. G. L. L. KEMMERLING, au cours d'un voyage d'exploration effectué en 1912, dans le bassin du fleuve Barito, au S. E. de l'île Borneo [1]). Ces fossiles, conservés au Musée géologique de la Technische Hoogeschool à Delft, m'ont été obligeamment communiqués par M. le Professeur G. A. F. MOLENGRAAFF, directeur de ce Musée.

Famille : RANINIDAE Dana 1852.
Genre : RANINA Lamarck 1818.
Sous-genre : LOPHORANINA Fabiani 1910.

Ranina (*Lophoranina*) *Kemmerlingi* nov. sp. (Fig. 1, 2a, b.).
= *Ranina* sp., in G. L. L. Kemmerling (l.c. p. 740, pas fig.).

Fig. 1.
Ranina sp. (schéma). — ½ grandeur naturelle.
Céphalothorax indiquant en grisé, la région à laquelle appartient le fragment décrit sous le nom. de R. KEMMERLINGI.

Les restes assez fragmentaires de cette espèce se réduisent à la partie droite de la région postérieure du céphalothorax et d'un article d'un péréiopode droit, probablement le troisième.

Les crêtes du céphalothorax, caractéristiques du sous-genre, sont disposées transversalement. Elles sont onduleuses, irrégulières, ne présentant aucun parallélisme et concaves vers l'avant, tout au moins dans la moitié postérieure du céphalothorax. Ces crêtes sont garnies en avant par un grand nombre de tubercules subépineux. Le bord du céphalothorax, souligné par un sillon, est granuleux ainsi que l'article, probablement un carpopodite, du péréiopode encore conservé.

[1]) G. L. L. KEMMERLING. Topografische en Geologische Beschrijving van het Stroomgebied van de Barito, in Hoofdzaak wat de Doesoenlanden betreft (Tijdschrift van het Koninklijk Nederlandsch Aardrijkskundig Genootschap, 2de ser., Deel XXXII, p. p. 575–641 & p. p. 717–774, carte et nombreuses figures dans le texte, Leiden 1915).

C'est une espèce de grande taille, dont les dimensions devaient atteindre celles que présentent souvent des formes actuelles, telles que *Ranina serrata* Lamarck des mers du Japon. Les autres repré-

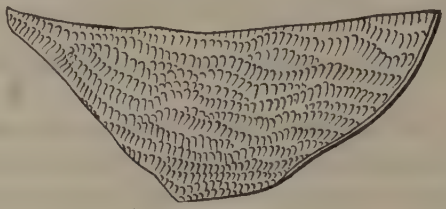

Fig. 2a.

Fig. 2b.

Ranina (Lophoranina) Kemmerlingi nov. sp. — Face dorsale.
2a. Fragment du céphalothorax. — Grandeur naturelle.
2b. Crêtes du céphalothorax. — × 3.

sentants fossiles du genre *Ranina*, dont l'espèce de Borneo se rapproche le plus par les caractères de son ornementation, sont :

Ranina laevifrons Bittner, du Lutétien du Vicentin,

R. Bittneri Loerenthey, du Bartonien du Vicentin et de la Hongrie,

R. Reussi H. Woodward, du Bartonien de la Hongrie,

R. Marestiana Koenig, du Priabonien du Vicentin,

R. porifera H. Woodward, de l'Oligocène inférieur de l'île Trinidad.

R. Kemmerlingi se distingue :

de *R. laevifrons* par ses tubercules arrondis à peine spiniformes,

de *R. Bittneri* par ses tubercules moins serrés et dépourvus de ponctuation,

de *R. Reussi* par ses crêtes plus nombreuses, plus serrées et ses tubercules moins distants,

de *R. Marestiana* par ses crêtes plus serrées et garnies de tubercules plus espacés mais plus volumineux,

de *R. porifera* par l'absence de ponctuation en avant des tubercules des crêtes.

Type. Musée géologique de la Technische Hoogeschool à Delft, échantillon No 6561 et 6562, empreinte et contre empreinte.

Gisement. Etage γ de R. D. M. Verbeek, probablement Oligocène.

Localité. Vallée du fleuve Barito (Borneo).

Famille : Calappidae Dana 1852.

Genre : Calappilia A. Milne Edwards 1873.

Calappilia borneoensis nov. sp. (Fig. 3).

Les marnes calcarifères avec débris de végétaux de l'étage β de R. D. M. Verbeek, renferment parfois de nombreux débris appartenant à un Brachyoure de petite taille. Ces restes toujours incomplets, sont à rapporter au genre *Calappilia* A. Milne Edwards.

La région frontale est étroite et se prolonge en avant par un faible rostre, les orbites semblent avoir été larges et peu profondes. Les sillons limitant une région gastro-cardiaque étroite sont peu profonds, les régions branchiales sont relativement étendues. La surface du céphalothorax est ornée de petits tubercules arrondis, d'autant plus saillants qu'ils sont plus rapprochés des bords, leur nombre augmentant dans les régions postérieures du céphalothorax. L'espace compris entre les tubercules est occupé par de fines granulations. Les bords latéraux rencontrent le bord postérieur sous un angle à peu près droit et se prolongent postérieurement, par une épine. La face sternale n'est pas connue.

Fig. 3. *Calappilia borneoensis* nov. sp. Face dorsale. × 2. Reconstitution à l'aide de fragments provenant de 5 individus.

Les fragments de céphalothorax sont accompagnés de débris de péréiopodes, trop morcelés pour qu'on puisse les décrire. Tout ce qu'il est possible de voir est que comparativement au corps de l'animal, ces péréiopodes étaient extrêmement développés. Jusqu' à présent, on ne possède pas d'autres renseignements sur les appendices du genre *Calappilia*.

Ces caractères sont suffisants pour distinguer cette forme, de toutes les espèces de *Calappilia* décrites jusqu'à ce jour. Le genre a été rencontré depuis l'Eocène moyen jusqu' à l'Oligocène moyen. On en connait les espèces suivantes:

Calappilia incisa Bittner, du Lutétien du Vicentin,
C. dacica Bittner, du Bartonien de la Hongrie,
C. verrucosa J. Boehm, de l'Eocène supérieur de Java,
C. perlata Noetling, du Tongrien du Samland,
C. vicetina Fabiani, du Tongrien du Vicentin,
C. sexdentata A. Milne Edwards et
C. varucosa A. Milne Edwards, du Rupélien de Biarritz.

L'espèce de Borneo se distingue de toutes les *Calappilia* sauf de *C. varucosa* A. Milne Edwards, par l'absence de nombreux tubercules spiniformes sur les bords latéraux du céphalothorax. Son ornementation la rapproche également de cette espèce de Biarritz,

elle s'en écarte cependant par ses tubercules plus saillants et moins également répartis sur toute la surface du céphalothorax. D'autre part, elle se distingue de *C. verrucosa* J. Boehm par son céphalothorax plus circulaire et quasiment hémisphérique.

Type. Musée géologique de la Technische Hoogeschool à Delft, échantillon No. 6563.

Cotypes. Echantillons No. 6564, 6565, 6566, 6567.

Gisement. Etage β de R. D. M. Verbeek = étage marneux (Mergeletage) = Eocène, probablement Lutétien.

Localité. 2 Kilomètres à l'Ouest de Kampong Lemoe (Borneo).

Neurology. — "*A partial foetus removed from a child.*" By Prof. C. WINKLER.

(Communicated at the meeting of June 30, 1923).

A few months ago a child of nearly three months, was brought in my clinic, having a fluctuating tumour in the neck and a not very intensive internal hydrocephalus.

Apparently it suffered from spina bifida, as the transverse processus of the 2d and 3d cervical vertebrae stood far apart and the processus spinosi were missing. The examination of the tumour made it probable that a myelo-cysto-cele might be found in it.

For the rest this healthy child had normal breathing, responded to pin-pricks with mimic facial expressions and spontaneously moved its four extremities.

The tumour, filled up with liquor, was opened by Dr. WALLER. He found in the middle of the fluid a strongly vasculated stalk, nearly 1 c.M. in diameter, connecting the deep tissues in the midline with the external wall of the tumour-cyst. After underbinding the stalk in the depth, he removed stalk and cystic tumour. In a week the child recovered. As I saw it again, six weeks after the operation, it appeared to be a rather normal child of circa five months of age.

The removed specimen was given to me.

A section made through the middle of the stalk proved, that it was a spinal cord surrounded by an intensely vasculated membrane (fig. 1*a*). In this spinal cord the columna posterior had disappeared and the dorsal wall of the central canal was open. The form of the central canal was as this figure shows.

The lateral, the anterior column and the grey matter were easily recognisable. In the lateral column the area of LISSAUER, the spino-cerebellar tracts and the surroundings of the grey substance are myelinisated. In the anterior funiculi was seen a strongly marrowed commissura anterior, and the tecto-spinal path has also gained marrow. Both, not medullated, pyramidal tracts are recognisable.

The substantia Rolando is strongly developed. The anterior horns contain atrophic large cells.

From this cord, ventral and dorsal medullated rootlets take origin.

Examining sections through the central end of the stalk (fig. 1*b*), the central canal widens. The lateral part of the medulla disappears and only a ventral rest of nervous tissue remains lined by the

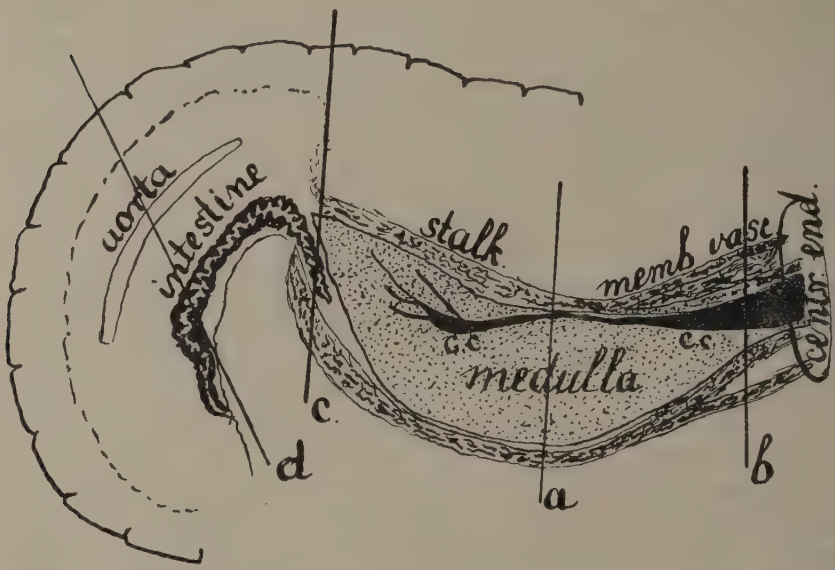

Fig. 1. Wall of the tumor and stalk.

ependyma of the central canal, now irregularly shaped and wound in an irregular way. The membrana vascularis also divides in two membranes, leaving a hole between them.

Examining sections through the stalk, towards its entrance in the skin (fig. 1*c*), the central canal soon closes dorsally. Its shape changes into another form, then it ends into many branches, one of which may be followed, lying excentrically, to the end.

At that moment the nervous tissue is represented by *a*. strongly medullated fibres of the medullar columns *b*. medullated posterior roots with well developed spinal ganglia (fig. 1*c*).

At the moment that the stalk reaches the skin, there is found, ventrally from what seems to me to be the caudal end of the spinal cord, a tube, which soon appears to be the intestinal tube.

Sectioning the wall of the tumour, caudally from the entrance of the stalk, it appears to contain the caudal end of an imperfectly developed, partly atrophied, foetus.

In foto 2 is seen, that cutis and subcutaneous tissue with hair-follicles and sudorific glands is separated from the new tissue by a system of lacunae, filled up with blood and bordered by endo-

Fig. 2. Foto from a section through the wall of the tumour (see fig. 1*d*.)

thelium-cells. Most striking however is the deeper part. A transverse section of a tube is found there, whose internal surface is irregularly wound.

It is formed by a single layer of cylindric epithelium, placed upon a membrana basilaris and bordered towards the lumen of the

tube by a transparent band with small transverse lines — a hem of cell-cilia. The loose connecting tissue, building the basilar membrane upon which the epithelium-cells repose, is surrounded by a transversal and by a longitudinal muscle-layer. I consider this tube to be the intestinal tube.

Dorsally from this tube are found the large vessels, aorta and vena abdominalis. In the foto (fig. I *d*) the section touches the left femur; at the right side the trochanter femoris is found. Also both ureters and more caudalward the bladder is seen.

In this way it appears that the wall of the tumour contains the caudal end of an insufficiently developed foetus, connected to the well developed child by a stalk, containing the caudal end of a medulla spinalis.

I presume a double monstrum, a duplicitas posterior is here present. The single head of this monstrum was followed by a double caudal part of the body. The one half of the body developed normally.

The other half atrophied. A relatively well developed medulla remained in the stalk, the caudal end of the foetus was found in the wall of the fluctuating tumour.

Hence this female child carried its atrophied twin-sister at her back. The superfluous atrophic foetus was removed and it is not impossible, that the remaining child may grow up normally.

ERRATUM.

On p. 310 of this volume line 13 from the top to omit the words *and Wolffian Ducts* and to read: by the kidney-tubules (TITSCHACK 1922, a. s. o.).